

Multi-element electrothermal AAS determination of 11 marker elements in fine ambient aerosol slurry samples collected with SEAS-II

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Abstract

Multi-element simultaneous electrothermal atomic absorption spectrometry (ETAAS) methods were developed for determining 11 elements, in three analytical groups (group-1, predominately crustal elements, Al, Cu, Fe, Mn, and Cr; group-2, tracers of coal and oil combustion as well as other anthropogenic sources, Se, As, Pb, and Ni; and group-3, tracers of municipal incinerator aerosol—Zn and Cd), in aqueous slurry of ambient fine airborne particles, collected, at 30 min intervals with the University of Maryland—Semicontinuous Elements in Aerosol Sampler-II (SEAS-II). Combined effects of acid (0.2% v/v nitric acid) and ultrasonic treatment (15 min) improved metals recovery and slurry stability. Linear calibration ranges were improved by using a 50 mL min⁻¹ carrier gas flow (mini-flow) during the atomization stage. However, analytical sensitivity for group-1 and 3 elements was compromised. Palladium (4 µg) and hydrogen (5% in Argon) were found to be effective modifiers for group-1 and 2 elements. A fast furnace temperature program was developed for group-3. Detection limits for the eleven marker elements by the SEAS-II-ETAAS approach were compared with traditional filter X-ray fluorescence, laser ablation-ICPMS, and instrumental neutron activation analysis (INAA) techniques used in air quality studies. The efficacy of the analytical method was evaluated by analyzing interim urban PM_{2.5} reference material, collected in Baltimore, by the National Institute of Standards and Technology (NIST) Gaithersburg, MD. Results obtained by the ETAAS methods agreed well with the results obtained by NIST using INAA.

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1. Introduction

Numerous studies suggest that ambient atmospheric particles are associated with severe health effects, including exacerbation of asthma, degradation of cardiopulmonary function, premature death, and cancer [1–3]. Studies also suggest that metals might, in-part, contribute to the adverse effects of particles by modulating the expression of pulmonary cytokines [4,5]. Primary particles, i.e., those emitted directly from sources, contain toxic elements but also markers useful in identifying their generic source types [6–9]. For example, As is a tracer of particles emitted from metals-ore processing; Se is nearly a unique tracer of coal combustion

aerosol; Ni and V are tracers of oil combustion aerosol; and fine-particle Fe and Mn are markers for steel mill emissions. Likewise, particles emitted from municipal incinerators contain percent levels of Cd and as much as 35% zinc chloride [8]. Primary particles from high-temperature combustion sources are typically smaller than 2.5 µm in diameter. Thus, determination of trace elements in ambient fine particles is essential for source apportionment and aerosol health effect studies.

Standard methods for determining elements in aerosol particles involve collection of particles on filters followed by analysis by X-ray fluorescence (XRF), atomic absorption spectroscopy (AAS), and more recently, inductively coupled plasma–mass spectrometry (ICPMS) [10]. In XRF methods, samples are analyzed directly, i.e., without dissolution or other treatment. However, sensitivities for many elements are inadequate to determine their concentrations in large per-

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centages of the filter samples collected. In AAS and ICPMS methods, the samples and substrates (e.g., filter) are usually digested prior to analysis. More recently, laser ablation has been used to introduce solid material captured on filter surfaces into ICP plasma for subsequent MS analyses [11,12]. However, the instability of laser output for continued operation, lack of suitable standards, and poor reproducibility due to the heterogeneity in both the sample and the filter matrix remain problematic in ablation techniques [10]. ICPMS has been little used for direct analysis of liquid suspensions, i.e. slurry samples, presumably due to clogging of the sample inlet capillary tube and deposition of particles on the walls of the spray chamber, water-cooled interface cones, and on the ion lenses.

Applications of direct slurry analysis with electrothermal atomic absorption spectrometry (ETAAS) for determination of metals have been increasing, as evident from the extensive literature published in the last decade [13]. The avoidance of sample preparation, in particular, total dissolution, is an important advantage of direct slurry analysis [13–15]. This methodology has been applied to atmospheric particles by at least a few workers [13,16–18]. Yu et al. [16] analyzed Pb in PM_{2.5} (particulate matter containing particles with aerodynamic diameters <2.5 μm) by ETAAS after dislodging particles collected on quartz filters into an acid solution. Terzieva and Arpadjan [17] analyzed atmospheric particles for Cd, Cr, Cu, Ni and Bi by AAS after dissolving the filter in organic solvent. Carniero et al. [18] reported a partial acid digestion method to extract airborne particles collected on quartz filters directly in the autosampler cup for analyses of Sb, V, and Ni.

The introduction of the echelle polychromator in atomic absorption instruments enables them to determine multiple elements at a time [19,20]. The Perkin-Elmer (PE) simultaneous multi-element electrothermal atomic absorption spectrometer (SIMAA 6000) is one of the successful multi-element instruments in the AA market at present [20–24]. A few papers have been published on the use of this instrument (For e.g., Cu, Mn and Mo in sea water [21]; Cu, Cr, Al, and Mn in human urine [22]; Pb, Ni, Sn and Cu in Al-alloys [23]; and several inorganic tracers urban in PM [24]). But to our knowledge, none has reported systematic and validated multi-element ETAA methods for fine airborne PM slurry samples.

In this communication, we report three multi-element ETAAS methods that have direct application to ambient fine PM slurry samples produced by the University of Maryland Semi-continuous Elements in Aerosol Sampler-II (SEAS-II; [24,25]). Determination of generic metal source markers such as Al, Fe, Cu, Cr, Mn, Pb, Ni, V, Ti, Se, As, Cd and Zn were of primary interest. V and Ti were excluded later as these two metals required rigorous furnace conditions to attain reasonable sensitivity. Remaining elements were grouped on the following basis: (i) minimal compromise in furnace temperature programming; (ii) absence of known atomic spectral overlaps within a group; and (iii) similar relative abundances of metals in urban fine aerosol particles. On these bases, Al, Cu, Fe, Mn,

and Cr, i.e., relatively non-volatile elements and primarily of crustal origin, constituted group-1. Minor metals, such as Se, As, Pb and Ni, in primary particles emitted from high temperature combustion sources, comprised group-2. Incinerator tracers such as Zn and Cd were analyzed together (group-3) as they required similar furnace temperature programming.

Furnace temperature programs and choice of matrix modifiers were evolved in such a way that they resulted in a wider linear dynamic range without strongly affecting analytical sensitivities. Utilization of end-capped tubes and a mini carrier gas flow during the atomization stage were also explored for this purpose. Stability of the SEAS-II slurry samples is also discussed herein. The effects of interferences of abundant constituents of ambient aerosols (specifically, sulfate, nitrate and chloride) and their tolerance levels on the elements of current interest were determined. The methods were validated by analyzing NIST-SRM 1640 (trace elements in rain-water) and the interim PM_{2.5} Reference Material (RM) from the National Institute of Standards and Technology (NIST), Gaithersburg, MD, USA. Method detection limits (MDL) of the SEAS-II-ETAAS approach are compared with the MDLs of existing methods in the literature for similar sample matrices.

2. Experimental

2.1. Apparatus

All measurements were performed using a PE (Norwalk, CT) SIMAA 6000 equipped with a transversely heated graphite atomizer (THGA), longitudinal Zeeman-effect background corrector, and autosampler (AS-72). End-capped and standard pyrolytic graphite-coated THGA graphite tubes were used, as needed. The SIMAA instrument was controlled by “AA Winlab” software version 2.3 (PE, Norwalk, CT). PE-hollow cathode lamps were used for all elements except for Se and As, for which electrodeless discharge lamps (PE, EDL2 systems) were used. The analytical wavelengths used in this study were as follows: Al: 309.3 nm; Fe: 248.3 nm; Cr: 357.9 nm; Cu: 324.8 nm; Mn: 279.5 nm; Zn: 213.9 nm; Cd: 228.8 nm; Pb: 283.3 nm; Ni: 232.0 nm; Se: 196.6 nm; and As: 193.7 nm. Integrated peak area of the atomic absorption signal was measured as a function of concentration.

The SEAS-II instrument has been described elsewhere [25,26]. Briefly, SEAS-II consists of a state-of-the-art dynamic aerosol concentrator mated to an automated sample collector. In SEAS-II, particles as small as 0.08 μm are grown to a size of 3–10 μm by condensation of water vapor using precisely metered steam injection. SEAS-II was used at four US air-monitoring “Supersites” (Baltimore, Pittsburgh, and St. Louis in 2001 and 2002; and the Bay Regional Atmospheric Chemistry Experiment-Sydney, Tampa in 2002). An inlet impactor with a 1.2 μm cut-point was used. Ambient air was sampled at 90 L min⁻¹ and samples were collected au-

tomatically in polypropylene vials, every 30 min. Collected samples were capped and stored in a cold room at -10°C . About 2000 samples have been analyzed, using the methods described in this communication.

2.2. Materials, reagents and solutions

High-purity deionized water (produced from a Milli-Q Plus system with QPAK2 filter cartridge, Millipore Corp, Bedford, MA) and baseline nitric acid ($\sim 70\%$ v/v, sub-boiling distilled, from Seastar Chemicals, Canada) were used throughout this study. Commercial multi-element standard solutions from Perkin-Elmer and Claritas Centriprep (Metuchen, NJ) were used for SIMAA instrument calibrations. All reagents were prepared in a horizontal HEPA filtered, laminar-flow, clean-air hood. Teflon and polypropylene containers were employed for the entire analysis. All sample containers, autosampler cups, and pipette tips were acid washed by immersion in 10% nitric acid (v/v) for 24 h, then rinsed several times with deionized water, and dried in laminar hood. A 0.2% (w/v) Pd solution was prepared by dissolving 0.2 g finely ground palladium metal (99.999% pure, Aldrich Chemicals) in 2 mL of nitric acid and 0.2 mL of HCl by closed-vessel microwave acid digestion. The solution was then heated on a hot plate to near dryness, and reconstituted with 0.2% nitric acid.

2.3. Interim PM_{2.5} RM slurry preparation

About 2 g of homogenized fine-urban particulate material (PM_{2.5}), collected at the Clifton Park site-Baltimore for use in NIST/EPA's PM_{2.5} inter-comparison SRM sample program, was dried at 110°C for 6 h. Then, about 0.05 g of dried sample was weighed to five significant figures into a clean 50 mL polypropylene vial using a Mettler Toledo AX105DR weighing scale. A known volume of 0.2% (v/v) nitric acid was added into the vial, capped, and sonicated for 15 min in a Branson-2510 model ultrasonic bath (100 W output power at 42 kHz). Further dilutions were carried out in 0.2% nitric acid immediately after ultrasonic treatment.

2.4. Microwave assisted total digestion of interim PM_{2.5} RM

Closed-vessel microwave-assisted wet decomposition of interim PM_{2.5} was performed using an MDS-205 microwave oven (1400 W, CEM Corp). A 0.1 g aliquot of the RM was weighed accurately into a PFA-lined digestion vessel, and 4 mL of concentrated nitric acid was added. The vessel was closed, placed inside the oven and the digestion was carried out in two steps (step-1: 6 min at 70% power; step-2: 4 min at 30% power, typically for four samples, i.e., three samples and a reagent blank). After cooling, the vessel cap was withdrawn, and the open vessel was placed on a hotplate kept inside a clean hood. Each sample was gently heated to near dryness, and subsequently transferred to a volumetric flask by

dissolving the residue with 0.2% (v/v) nitric acid. Digested sample solutions were diluted with 0.2% nitric acid solution as needed for the analysis.

2.5. Analysis start-up conditions

Several 30 min slurry samples, collected before the start of the field studies, were homogenized and used as test slurry for the optimization of graphite furnace temperature programs. A mixture of 4 μg of Pd and 10 mg of magnesium nitrate (universal modifier), and argon purge gas were used for preliminary studies of all groups. Standard THGA graphite tubes and default furnace steps, recommended in the SIMAA product literature [27] and Winlab software were used as the starting point to evolve the best possible furnace conditions for the simultaneous determinations of elements in each of the three analytical groups. The wash solution (usually water) used to rinse the injection capillary was replaced with a mixture containing 0.5% v/v nitric acid and 0.005% v/v Triton X-100 solution to prevent particles from sticking on the injection tip.

2.6. Slurry analysis

Frozen samples were thawed and sample volume was determined by gravimetry (assuming a slurry density of 1 g mL^{-1}). A 10 μL aliquot of $\sim 69\%$ nitric acid was dispensed for every 3.5 mL of sample in the vial to adjust the final acid concentration of the slurry to $\sim 0.2\%$ (v/v). Then, the sample vials (20 at a time) were placed in an ultrasonic bath for 15 min. One milliliter aliquots of freshly sonicated slurry were transferred to pre-acid-washed and dried disposable autosampler vials and loaded on the autosampler for analysis. Each sample was analyzed in three replicates, and the integrated absorbance values were recorded. Aqueous standards were used to construct calibration curves. A linear curve fit was used to interpolate sample concentrations.

3. Results and discussion

3.1. Furnace conditions and calibration for group-1

The effects of matrix modifiers on group-1 metals were studied with the furnace conditions recommended by PE. In the presence of a universal matrix modifier (10 mg of magnesium nitrate and 4 μg palladium), atomic absorbance signals for Al, Cr, and Fe increased relative to matrix modifier-free determinations, by 30, 10 and 21%, respectively, while those for Mn and Cu were unaffected. When 10 mg of magnesium nitrate was used as a modifier, absorbances for all elements were unaltered, except for Al, for which the absorbance signal increased only by 9%. The integrated absorbance of Cr decreased by 35% when 4 μg Pd was used as a modifier. Addition of a reducing agent, such as ascorbic acid, to the palladium nitrate is a conventional way of improving the ef-

efficiency of palladium [28]. Hydrogen gas has also been used for this purpose [22,29]. Therefore, a mixture of 5% hydrogen in argon was used as a second carrier gas, and introduced after the first dry step of the furnace program. This improved integrated absorbances for Al, Cr and Fe by 4, 40 and 9%, respectively. This observation, as reported by Lin and Huang [22], suggests that in situ pre-reduction of Pd ions by H₂ yielded metallic palladium which is conducive to metal–Pd interaction, and in turn facilitated uniform and efficient atomization for Cr, Al and Fe. Also, pre-reduced palladium is found to be one of the best modifiers for Cr. The absorption signals for all elements (100 pg, each) remained approximately constant after Pd additions ranging from 1 to 8 µg; and hence, 4 µg were used.

Pyrolysis (for removal of organic matrix matter) and atomization temperatures are critical parameters in air particulate matter analysis, especially when elements of varying volatility are analyzed simultaneously. A 20 µL test slurry was injected and the dependences of integrated absorbances of Al, Cr, Mn, Cu, and Fe on the ashing temperature were studied between 300 and 1600 °C, at a constant atomization temperature of 2300 °C, and with the matrix modifier of 4 µg of Pd and 5% H₂ in Ar during dry step-2. Background absorbances decreased sharply between 400 and 600 °C for Al, Cu, and Fe; and, only slight and gradual reductions were observed for these elements as the ash temperature was raised above 600 °C. Atomic signals remained approximately constant in the range of 600–1400 °C for Al, Fe and Cr, and 500–1200 °C for Cu and Mn. Therefore, 1150 °C was chosen for pyrolysis.

The effect of atomization temperature was studied between 1700 and 2500 °C at the chosen pyrolysis temperature. Maximum and consistent absorbance was measured between 2350–2500 °C for Al; 1900–2300 °C for Fe; 2300–2400 °C for Cr; and 1900–2400 °C for Cu and Mn. With small compromise on Fe sensitivity (about 5% loss), 2350 °C was chosen as the atomization temperature for the simultane-

ous determination of group 1 elements. Table 1 summarizes furnace temperature steps evolved from the optimization study.

Once the optimized furnace conditions were determined, calibration plots were constructed using standard THGA tubes. The calibration curve of Cr contained two distinct linear sections as observed by Bencs et al. [30]. In addition, short linear ranges exhibited by Al, Fe, and Mn necessitated further improvements in the method. Deviations from linearity at higher concentrations in ETAA studies can be attributed to the increased diffusional loss of analyte at higher concentrations. Diffusion coefficients for each element vary with temperature. Usage of end-capped THGA tubes (tubes with cylindrical restrictions at their ends) or a carrier gas flow of about 50 mL min⁻¹ during atomization has been suggested as possible ways to improve calibration linearity [20,30]. A small carrier flow during the atomization stage is often used to regulate atomic vapor loss. Such a “mini-flow” condition sometimes results in wide linearity but at the expense of analytical sensitivity. End-capped tube restricts diffusional loss of atomic vapor and thereby, increases the transient atomic cloud density inside the tube, which in turn results in enhanced sensitivity. It should also be noted that the SIMAA atomizer, itself, does not operate in a true “gas stop” mode; an unknown micro-flow of carrier gas is always present during the atomization step. Therefore, finding an optimum setting associated with a minimal and controlled loss of atomic vapor is imperative for simultaneous multi-element determinations.

With standard THGA tubes, a 50 mL min⁻¹ (mini-flow) of purge gas during atomization eliminated double sloping of Cr, but at the expense of its analytical sensitivity. Mini-flow conditions extended the upper limit of linear ranges of Al and Cr while no effect was noticed for Fe and Mn. Application of end-capped tubes did not require a mini-flow to remove double sloping of Cr, but affected the linearity of Al severely. Mini-flow application when end capped tubes were used, re-

Table 1
Furnace heating programs for all groups

Group	Furnace step	Furnace temperature (°C)	Ramp time (s)	Hold time (s)	Internal flow (mL min ⁻¹)	Gas type	Signal read
1	1. Dry-1	110	1	25	250	1	0
	2. Dry-2	130	20	25	250	1	0
	3. Ash	1150	15	20	250	0	0
	4. Atom	2350	0	5	50	0	1
	5. Clean	2550	1	5	250	0	0
2	1. Dry-1	110	5	25	250	0	0
	2. Dry-2	130	5	10	250	1	0
	3. Ash-1	900	10	10	250	1	0
	4. Ash-2	900	1	15	250	0	0
	5. Atom	2250	0	5	0	0	1
	6. Clean	2500	1	5	250	0	0
3	1. Dry	250	35	10	250	0	0
	2. Atom	1800	0	5	50	0	1
	3. Clean	2400	1	3	250	0	0

Gas Type: 0 indicates Ar carrier; 1 indicates 5% H₂ in Ar carrier. Signal: 1- atomic absorbance measured. Injection volume: 20 µL for group-1; 10 µL for group-3; 20 + 20 µL for group-2.

sulted in significant improvements in the linear upper ranges for Fe, Al and Cr. Linear range, slope, and regression values for analyses of all group-1 elements with standard and end-capped THGA tubes under both stop-flow and mini-flow conditions are presented in Table 2. As can be seen from this table, the ultimate sensitivity of end-capped THGA with mini-flow is comparable to standard THGA with stop flow conditions; hence, analytical measurements are not compromised.

3.2. Furnace conditions and calibration for group-2

Among the platinum group metals, Pd has been shown to be the most efficient modifier for the removal of sulfate matrix interference in the determination of Se and As, so it was chosen for this group [31]. The effect of ash and atomization temperature on the atomic and background absorption signals were studied with the 4 μg Pd modifier/5% H_2 in Ar purge gas during drying and ashing steps, as described above. From the pyrolysis curves it is apparent that As, Pb and Se were stabilized at pyrolysis temperatures below 1400, 1000, and 1200 $^\circ\text{C}$, respectively (Fig. 1). While Ni, a refractory element, did not require a modifier for stabilization, its ill-defined broad transient atomic peak (baseline peak width ~ 2.5 s) improved to a well-defined peak (baseline peak width ~ 2 s) in the presence of Pd/ H_2 . Appreciable reduction in the background absorbance was not noticed in the temperature range of 700–1200 $^\circ\text{C}$ for any of the elements. Therefore, 900 $^\circ\text{C}$ was deemed to be optimum, hence atomization temperature was studied at this temperature, (Fig. 1). Lead was released early and displayed broad atomic peaks in the temperature range of 1800–2000 $^\circ\text{C}$. Its peak width narrowed as the atomization temperature was increased. A plateau for all elements were observed between 2150 and 2350 $^\circ\text{C}$, hence, 2250 $^\circ\text{C}$ was taken as the optimum atomization temperature.

When the 5% H_2 was not fully purged before atomization, Se signals decreased by 16%. This has been attributed to the formation of volatile selenium hydride [29]. Therefore, an additional pyrolysis step with argon purge was introduced. It was noted that at least 10 s of purging was essential to flush out H_2 completely in order to regain the actual integrated absorbance of Se. Therefore, a two-stage pyrolysis with 5% H_2 for 10 s and 100% argon for 15 s was set. As such, the 5% H_2 did not show any influence on the transient atomic peaks of As, Se and Pb. However, its use was necessitated by its ability to reduce the chloride matrix interference on Se (Section 3.5).

The effect of the modifier mass on the group-2 metals was studied. It was found that the minimum amount of Pd necessary for quantitative stabilization of 200 pg each of Se, Pb and As was 0.5 μg . The integrated absorbance remained constant for all elements up to 20 μg of Pd. Therefore 4 μg was subsequently used.

End-capped tubes were preferred for group-2 elements, as these resulted in 2.0, 2.1, 1.7, and 1.5-fold enhancements in analytical sensitivities (as compared to standard THGA) for

Table 2
Slopes and linear dynamic ranges obtained at different conditions for group-1 elements

	Standard THGA tube						End-capped THGA tube					
	Stop flow			Mini flow			Stop flow			Mini flow		
	Linearity (ng mL ⁻¹)	Slope ($\Delta\text{signal}/\Delta\text{ng mL}^{-1}$)	R	Linearity (ng mL ⁻¹)	Slope ($\Delta\text{signal}/\Delta\text{ng mL}^{-1}$)	R	Linearity (ng mL ⁻¹)	Slope ($\Delta\text{signal}/\Delta\text{ng mL}^{-1}$)	R	Linearity (ng mL ⁻¹)	Slope ($\Delta\text{signal}/\Delta\text{ng mL}^{-1}$)	R
Al	0.2–15 40–100	0.0029 0.0004	0.9999 0.9977	0.5–20	0.0019	0.9898	0.2–10	0.0042	0.9898	0.2–40	0.0021	0.9991
Cr	0.2–8.0 12.0–60	0.0105 0.0067	0.9999 0.9989	0.3–20	0.0077	0.9995	0.1–8.0	0.0142	0.9995	0.1–30	0.0076	0.9997
Cu	0.5–100	0.0031	0.9979	0.4–100	0.0027	0.9995	0.2–20	0.0041	0.9998	0.2–100	0.0024	0.9995
Fe	1.0–8.0 20–80	0.0051 0.0031	0.9999 0.9959	0.6–8.0	0.0043	0.9989	0.5–4.0	0.0074	0.9992	0.6–30	0.0043	0.9989
Mn	0.4–8.0 20–60	0.0106 0.0033	0.9974 0.9955	0.4–8.0	0.0088	0.9998	0.2–8.0	0.0167	0.9992	0.2–12	0.0091	0.9993

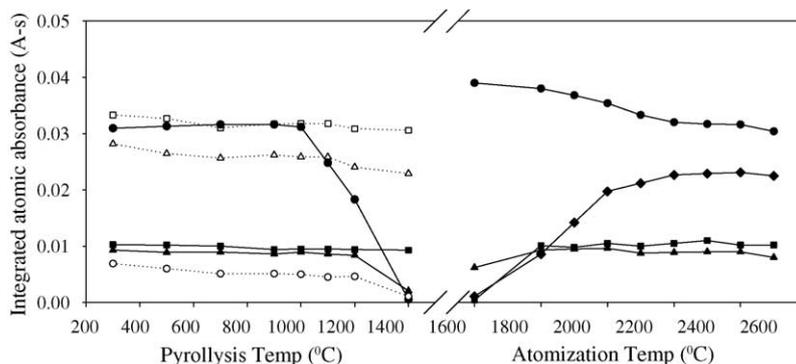


Fig. 1. Pyrolysis and atomization temperature study of group-2. (■) As signal; (△) As background; (◆) Ni signal; (◇) Ni background; (●) Pb signal; (○) Pb background; (▲) Se signal; (△) Se background.

As, Se, Pb and Ni. A sample volume of 40 μL was chosen to increase the mass for analysis for minor elements in the slurry sample. But larger sample volume affected analytical precision, which was mainly due to sample spread in the graphite tube. Therefore, two step sample injections, 20 μL each, the second after dry step-2, were followed.

Linearity, correlation coefficient (R), and slope ($\Delta\text{signal}/\Delta\text{ng mL}^{-1}$) of the group-2 elements were studied. With end-capped tubes and stopped purge flow during atomization, the following results were obtained: Se (linearity: 0.3–40 ng mL^{-1} , $R = 0.9999$, slope = 0.0020), As (linearity: 0.2–40 ng mL^{-1} , $R = 0.9999$, slope = 0.0036), Pb (linearity: 0.3–40 ng mL^{-1} , $R = 0.9999$, slope, 0.0022) and Ni (linearity: 0.5–20 ng mL^{-1} , $R = 0.9997$, slope = 0.0052). It was interesting to note that with mini-flow during atomization, while upper limits of linear ranges were extended by factors of 2.5, 2, 3, and 2, their analytical sensitivities were only slightly compromised, i.e., by factors of 0.93, 0.88, 0.89 and 0.88 for Se, As, Pb and Ni, respectively. It appears as though the diffusional loss for heavier elements in end-capped tubes is minimal, and in such instances, the mini-flow during atomization acts more as a medium to evenly disperse the atom cloud inside the tube.

3.3. Fast furnace programming and calibration for group-3

The effect of the drying temperature on the integrated absorbance was studied at an atomization temperature of 1800 $^{\circ}\text{C}$ and stop-flow during atomization. As seen in Fig. 2, atomic signals were maximum between 150–400 $^{\circ}\text{C}$, and 100–300 $^{\circ}\text{C}$, for Cd and Zn, respectively. Therefore, 250 $^{\circ}\text{C}$ was chosen. Drying time was varied between 5 and 60 s, and noted that a minimum of 10 s was required to attain a reasonable precision. A 35 s ramp time and 10 s drying time resulted in a precision of less than 2% (RSD) for both Cd and Zn, and hence were subsequently adopted.

Effects of modifiers (including magnesium nitrate, palladium nitrate, and ammonium mono hydrogen phosphate) were studied, individually, on the atomic signals of Cd and Zn. Pd gave high background for Cd and hence it is not suitable for this group. Precision and integrated absorbance for Cd and Zn were not affected significantly with ammonium hydrogen phosphate. In the presence of magnesium nitrate, atomization of Zn was delayed (about 0.5 s for the peak maximum) due to Mg–Zn interaction. As can be seen in Fig. 3, the Zn peak is broadened and the signal height is decreased, although the integrated area remains almost the

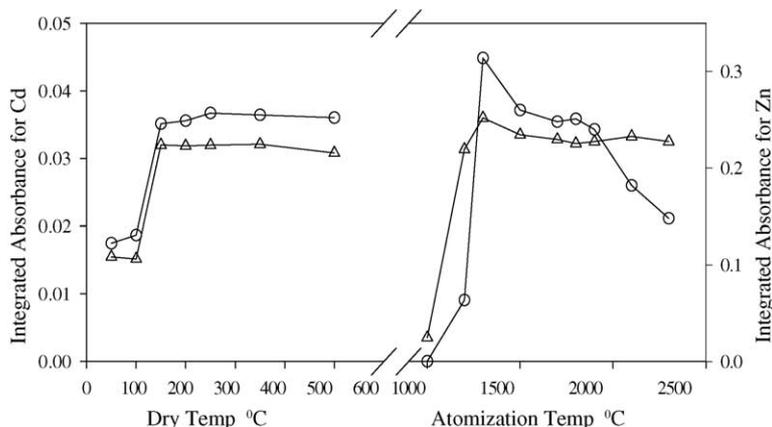


Fig. 2. Dry and atomization temperature study of group-3. Atomic absorbance signal of Cd (denoted as Δ) and Zn (denoted as \circ).

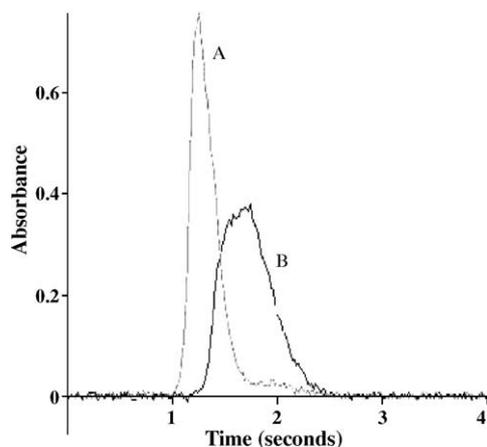


Fig. 3. Atomic peak of Zn with (B) and without (A) magnesium nitrate modifier.

same. As a result, precision was improved by using the magnesium nitrate modifier (i.e., 0.6% and 2.5% RSD with and without modifier, respectively, for 100 pg of Zn). A similar peak broadening effect for Cd was also noted and the magnesium nitrate modifier likewise improved precision by 0.9% and 1.5% with and without the modifier for 20 pg of Cd. Absorbance signals for Cd and Zn were unaffected in the range of 5–15 μg of $\text{Mg}(\text{NO}_3)_2$ and hence, 10 μg was adopted.

Atomization temperature was varied in the range 1300–2400 $^\circ\text{C}$ (Fig. 2). Cadmium absorbance was maximum in the range 1500–2300 $^\circ\text{C}$, whereas the integrated absorbance of Zn was maximum only in the range 1650–1850 $^\circ\text{C}$. Therefore, 1800 $^\circ\text{C}$ was retained as the atomization temperature.

Calibration curves were constructed with the conditions specified above. Cadmium exhibited linearity in the range of 0.3–12 ng mL^{-1} (slope of 0.0178; $R=0.9946$), and Zn; 0.1–15 ng mL^{-1} (slope of 0.0298; $R=0.9999$). With a mini-flow of 50 mL min^{-1} during atomization, linear ranges were extended further and with better correlation for both the analytes (Cd: 0.3–20 ng mL^{-1} , slope = 0.0122, $R=0.9995$; Zn: 0.3–30 ng mL^{-1} , slope = 0.0171, $R=0.9992$). Analytical sensitivities were compromised, as the much-needed wide linear range for Zn, and better correlation for Cd were achieved with the mini-flow during atomization. The total cycling time of the developed program is just 53 s; hence, more sample throughput is achieved as compared to the normal program cycle of 120 s. Optimized furnace steps are summarized in Table 1.

3.4. Sample homogeneity and pre-treatment

In SEAS-II, sub-micrometer aerosol particles are forced to grow to between 3 and 8 μm with water vapor, by condensation [25,26], prior to concentration in the virtual impactor. This results in a fairly stable and homogenized slurry, composed of water-soluble components and non-soluble soot and

dust particles. Preliminary studies indicated that no significant differences could be observed between the results of elemental analysis of freshly collected samples, analyzed before and after pre-treatments i.e., ultrasonication and acidification (discussed below). Freshly collected slurry samples were found to be stable for more than 6 h for Al, Cr and Fe, and 24 h for As, Cd, Mn, Pb, Se and Zn. On standing for longer periods, especially under freezing conditions (the recommended method of storage of field samples for off-line chemical and biological assays) insoluble portions of collected particles agglomerate and settle visibly at the bottom of the vials in a few days. This necessitated sample pre-treatment prior to analysis.

The effects of ultrasonic treatment and acidification with nitric acid on the slurry samples were examined as follows. The effect of nitric acid concentration on slurry stability and elemental recovery was studied using a 15 min ultrasonic treatment. In the concentration range of 0.05–5% HNO_3 , integrated absorbances for As, Cd, Cu, Pb, Mn, Se and Zn were almost constant. Al, Cr and Fe required an acid concentration of above 0.1% for maximum recovery. Ultrasonic agitation time was investigated with test slurry containing 0.2% nitric acid and it was found that 10 min of ultrasonication was sufficient to attain maximum recovery for all elements studied. We also observed that slurry stability was increased as the concentration of nitric acid was increased. For example, As, Ni, Pb and Se concentrations in slurry samples that were heavily influenced by coal combustion aerosol, were stable for only 30 min at 0.05% acid concentration; whereas 12 h stability resulted with 2% acid concentration. For a 0.2% acid, integrated absorbance remained stable for 6 h for As, Cd, Cu, Pb, Se and Zn, and 3 h for Al, Cr, Fe and Ni. Triton X-100 and glycerin (final concentration of 0.005%) were studied, individually, as stabilizing agents. With Triton X-100, aluminum and iron concentrations were stable for about 6 h. But it was not recommended as sufficient stability has already been obtained with nitric acid and blank corrections would be needed with Triton X-100 and glycerin as these reagents are not commercially available in ultrahigh purity.

There have been reports that slurry sampling ETAAS gives incomplete recovery [32]. Larger particles vaporize slowly in the graphite furnace resulting in incomplete atomization of analytes. Additionally, these particles may be less efficiently pipetted as a slurry of larger particles is less likely to be remain homogeneous. Sedimentation is less pronounced for low-density particles. Introduction of slurry samples with high solids content into the graphite tube has been shown to increase background absorbance signals and sometimes affect analyte signals severely. With SEAS-II, the mass of particles collected in the size range of 50 nm to 1.2 μm lies at microgram levels for a 30 min collection period. At such low solid contents, optimization of slurry concentration has not been critical. However, sample dilutions were sometimes unavoidable as the chemical composition of particles changes with particle source characteristics.

3.5. Interference study

In Baltimore, concentrations of atmospheric PM_{2.5} typically ranges between 20 and 80 $\mu\text{g m}^{-3}$. This material contains substantially larger amounts of substances that may potentially interfere with the metals analyses (e.g., ammonium sulfate, 4–60%; ammonium nitrate, 0.6–15%; and chloride, <5% [33]). Herein, the effects of ammonium sulfate, ammonium nitrate, and sodium chloride concentrations on the determination of elements of interest were studied. We define the tolerance level as the amount that causes a $\pm 5\%$ error in the determination. To determine the tolerance levels, we introduced a known quantity of the analyte (these ranged from 20 to 100 pg) and increased amounts of one of the interferants until a deviation of $\pm 5\%$ was observed. Amounts of analytes and the corresponding maximum interferant mass tolerated are shown in Table 3. Park et al. [33] report ammonium sulfate, ammonium nitrate, and sodium chloride concentrations of 60, 15, and $\sim 5 \mu\text{g m}^{-3}$ of in urban PM_{2.5}, respectively, during summer haze and stagnation episodes. This corresponds to 162, 40.5, and 13.5 μg of ammonium sulfate, ammonium nitrate, and NaCl in a 30 min SEAS-II sample whose average slurry volume is 5 mL. Thus, 324, 81, and 27 ng of ammonium sulfate, ammonium nitrate, and NaCl would be introduced along with the analytes into the furnace for a 10 μL sample injection.

The severity of the interference depends on the ratio of the interferant to the analyte. Therefore, tolerance ratios are derived and included in Table 3. For comparison, we also list interferant-to-analyte ratios relevant to urban PM_{2.5}. These were calculated conservatively, by choosing interferant levels present during pollution episodes, i.e., when the interferants are at their maximum concentrations. Appropriate levels of the elements are taken to be their lowest frequently observed concentrations. ETAA-instrument detection limits (IDL) are taken as the lowest concentrations for Se, As, Pb and Ni as these elements were frequently measured at their

IDL. It can be seen from Table 3 that the observed tolerance ratios are at least 30–100 times higher than their respective ratios in PM_{2.5} during the urban pollution episodes. Tolerated ammonium sulfate-to-Se ratios were close to the pollution episode ratio, but this is an unlikely condition (i.e., the highest sulfate level when Se at the instrument detection limit) as sulfates originating from fossil fuel combustion contains elevated levels of Se [6–8]. Hence, the developed methods can be safely applied to fine PM slurry samples.

It has been reported that introduction of H₂ gas during the ash step minimizes chloride interferences [29]. However, except for Se, we did not observe significant improvements to the tolerance level of chloride for any of the elements. Also, under the optimal conditions, all elements tolerated nitric acid concentrations up to 10% (v/v).

3.6. Detection limit

ETAA-Instrument detection limits are given as three standard deviations of nine successive replicates of the reagent blank, which is a mixture of 0.2% nitric acid solution and the matrix modifier. The values are 4.4, 1.8, 1.8, 2.2, 13.4, 1.3, 1.5, 12.1, 8.2, 12.8, 16.1 pg for Al, Cr, Mn, Cu, Fe, Cd, Zn, Se, As, Pb and Ni, respectively. To calculate the SEAS-II-ETAAS method detection limits, a HEPA filter capsule was connected to the SEAS sampling inlet and air was sampled. Since particles were removed by the HEPA filter, sample volume produced in 30 min was negligible (~ 0.3 mL). Therefore, four successive samples were combined for analysis. In principle, there should not be any slurry production when there are no particles in the system. Hence, the measured concentration was regarded as originating from leakage through the HEPA filter and possibly various instrument seals and, thus, included in the DL calculation. The method detection limit was given as the concentration of the metal in the blank plus three times the error (propagated from analytical results, slurry collec-

Table 3
Tolerance levels of salts

Element ^a	Amount tolerated (μg)			Tolerated salt to analyte ratio $\times 10^{-3}$			Pollution episode urban PM _{2.5} salt to analyte ratio $\times 10^{-3}$		
	(NH ₄) ₂ SO ₄	NH ₄ NO ₃ ^b	NaCl	(NH ₄) ₂ SO ₄	NH ₄ NO ₃ ^b	NaCl	(NH ₄) ₂ SO ₄ 60 $\mu\text{g m}^{-3}$	NH ₄ NO ₃ ^b 15 $\mu\text{g m}^{-3}$	NaCl 5 $\mu\text{g m}^{-3}$
Al (100 pg)	400	400	400	4000	4000	4000	5	1	10
Cr (20 pg)	100	400	800	5000	20000	40000	13	3	4
Mn (20 pg)	200	400	400	10000	20000	20000	13	3	4
Cu (50 pg)	200	400	800	4000	8000	16000	11	3	5
Fe (20 pg)	100	400	800	5000	20000	40000	2	0	30
Se (100 pg)	10	400	1 ^c , 10	100	4000	100	107	27	1
As (100 pg)	500	400	50	5000	4000	500	158	40	1
Pb (100 pg)	500	400	50	5000	4000	500	101	25	1
Ni (50 pg)	500	400	100	10000	8000	2000	80	20	1
Cd (20 pg)	100	100	10	5000	5000	500	5	1	6
Zn (100 pg)	50	100	10	500	1000	100	4	1	7

^a Amounts in parenthesis are those used for tolerance level studies.

^b Maximum tolerance level not studied. Furnace conditions are those specified in Table 1.

^c Amount tolerated when hydrogen was not used as modifier.

Table 4

Method detection limits of elements obtained by the present method in comparison with those given by XRF, LA-ICPMS and INAA methods, and the yearly average concentration in Baltimore

Elements	SEAS-II-ETAAS (ng m ⁻³)	INAA [35] (ng m ⁻³)	LA-ICPMS [36] (ng m ⁻³)	XRF [34] (ng m ⁻³)	Yearly average ± S.D. in Baltimore [34] (ng m ⁻³)
Al	3.80	5.5	1.67	195	45 ± 68
As	0.03	1.4	0.08	23.2	2.0 ± 1.5
Cd	0.04	32		109	5.0 ± 4.4
Cr	0.05	3.0	0.33	19.8	1.9 ± 1.4
Cu	1.07	35	11.7	22.5	5.6 ± 4.5
Fe	0.72	20	2.51	22.8	144 ± 99
Mn	0.14	0.4	1.34	21.1	4.4 ± 3.5
Ni	0.18	N.D.	0.08	16.5	2.7 ± 2.1
Pb	0.31	N.D.	0.04	49.2	6.4 ± 4.5
Se	0.02	2.5	0.05	27.9	2.5 ± 1.7
Zn	7.15	3.2	2.51	22.5	28 ± 33

tion efficiency, and air volume). Calculated values are given in Table 4.

Method detection limits for elements obtained by XRF (as reported by the commercial lab for speciation samples) [34], INAA [35], LA-ICPMS [36], and the daily average concentrations in the Baltimore area (average of daily concentrations measured in 2002) [34] are summarized in Table 4. As indicated, the SEAS-II-ETAAS method detection limits for elements are considerably lower than those reported for XRF and INAA. Furthermore, they are well below the concentrations in ambient PM_{2.5} in Baltimore. Therefore, reliable metals measurements can be made using SEAS-II-ETAAS.

3.7. Methods evaluation

The proposed simultaneous multi-element methods have been employed for the analysis of NIST SRM 1640 (trace metals in rain water). The SRM 1640 was diluted five times for the analyses. As indicated in Table 5, there is good

agreement between our measured values and those certified by NIST. The mean of three replicate analyses and the 95% confidence intervals (*t*-student = 4.30) are reported. To evaluate the accuracy of the fine-particle slurry method, the interim PM_{2.5} RM, collected by NIST in Baltimore, was analyzed by both slurry sampling and total digestion methods. The multi-element-ETAAS results obtained for both the sample treatment methods are presented in Table 5. Absence of statistically significant differences between the mean values at *P* = 0.05 was observed for all elements except for Ni.

Slurry analysis results were also compared with the available INAA results obtained by NIST. As indicated in Table 5, no appreciable differences could be observed for the two methods. This demonstrates the absence of matrix interferences in the ETAAS slurry method. We note that the concentrations of Ni, Cr and Fe in the interim PM_{2.5} RM are substantially greater than those found in typical urban fine PM samples. An independent electron microprobe study on

Table 5

Analytical results of SRM 1640 and anticipated fine particles SRM obtained from the developed methods

Element	SRM1640		NIST interim reference material PM _{2.5}		
	Certified values (ng mL ⁻¹)	Found values ($\bar{x} \pm t\sigma/\sqrt{n}$) (ng mL ⁻¹) ^a	INAA method ($\bar{x} \pm 1\sigma$) (mg g ⁻¹) ^b	Acid digestion method ($\bar{x} \pm 1\sigma$) (mg g ⁻¹)	Slurry-ETAAS analysis ($\bar{x} \pm 1\sigma$) (mg g ⁻¹)
Al	52.6 ± 1.5	49.8 ± 2.5	53.9 ± 0.4	52.6 ± 3.3	51.9 ± 3.6
Cr	38.6 ± 1.6	40.2 ± 2.2	46.8 ± 0.8	43.7 ± 0.3	42.7 ± 0.5
Mn	121.5 ± 1.1	120.0 ± 7.2	2.8 ± 0.1	2.5 ± 0.3	2.1 ± 0.1
Fe	34.3 ± 1.6	34.2 ± 2.5	195 ± 4	202 ± 5	201 ± 3
Ni	27.4 ± 0.8	28.3 ± 1.7		16.9 ± 0.4	13.6 ± 0.7

Element	SRM1640		NIST interim reference material PM _{2.5}		
	Certified values (ng mL ⁻¹)	Found values ($\bar{x} \pm t\sigma/\sqrt{n}$) (ng mL ⁻¹) ^a	INAA method ($\bar{x} \pm 1\sigma$) (μg g ⁻¹) ^b	Acid digestion method ($\bar{x} \pm 1\sigma$) (μg g ⁻¹)	Slurry-ETAAS analysis ($\bar{x} \pm 1\sigma$) (μg g ⁻¹)
Cu	85.2 ± 1.2	87.1 ± 6.2		463 ± 10	438 ± 11
Se	21.9 ± 0.5	20.9 ± 1.5		47.7 ± 3.8	47.2 ± 2.3
As	26.7 ± 0.4	27.0 ± 1.3	40.1 ± 2.1	38.3 ± 2.9	39.0 ± 4.4
Pb	27.9 ± 0.1	28.5 ± 1.3		140 ± 12	147 ± 10
Cd	22.8 ± 0.9	21.4 ± 0.6		22.9 ± 0.7	24.4 ± 1.2
Zn	53.2 ± 1.1	51.8 ± 0.9	630 ± 170	616 ± 12	596 ± 7

^a 95% confidence interval (*n* = 3).

^b Carried out at NIST-Gaithersburg, MD.

the interim RM revealed severe contamination of the RM with stainless steel particles from a stainless steel cyclone used to isolate the fine particles [35]. It is likely that the deviation observed was related to lower atomization efficiency for Ni in metallic steel particles. In any event, metallic steel particles are not the major constituents of urban fine PM, and thus significant differences between the slurry and digestion methods cannot be taken as the failure of the developed method.

4. Conclusion

Direct, simple, yet precise and accurate ETAAS methods have been developed for important marker elements in atmospheric fine particle slurry samples produced by the University of Maryland Semicontinuous Elements in Aerosol Sampler (SEAS) II. Nearly 2000 samples collected at four US advanced air-pollution monitoring sites (“supersites”) have been successfully analyzed [26]. Due to the limited dynamic range of AA and non-availability of less sensitive analytical wavelengths employed for multi-elemental analysis with the SIMAA 6000, dilution was often required for samples that were influenced by the local and regional pollution episodes. However, the linear range and detection limits for group-2 elements are adequate for any ambient environmental aerosol samples collected in the above-mentioned “supersite” studies. This suggests that SEAS-II could be successfully mated to the multi-element ETAAS for on-line determination of Se, As, Pb and Ni, thus permitting near-real time temporal concentration profiles to be developed for these elements. The number of elements and sample throughput by ETAA methods are poorer than either ICPMS or XRF, but detection limits are far better than those typically reported by XRF and the purchase cost of the ETAA is substantially lower than ICPMSs.

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