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Uncertainty of high resolution inductively coupled plasma mass spectrometry based aerosol measurements

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ABSTRACT

Simultaneous and multi-elemental method was optimized to determine 35 elements in 274 coarse and fine aerosol samples by using HR-ICP-MS. The procedures were validated. Measurement uncertainties of all elements including sampling uncertainties were calculated by applying bottom-up approach. The average recoveries obtained for each element ranged between 79% and 129% using NIST SRM 1648, urban dust. The calculated uncertainties of the analytical methods were between 2.9% and 18% for both sample types. The major contributions to the uncertainty budget come from the calibration curves, repeatability and volume of air.

1. Introduction

Trace element concentrations in atmospheric aerosols are now widely used in source-receptor modeling studies. To obtain such large data set, it is important to choose cost and time effective method for both sample preparation and analysis. The reagents chosen must digest the sample as completely as possible and keep the elements stable in solution. Nitric acid and hydrochloric acid mixtures can accomplish this for many elements but they cannot completely digest silicon-containing compounds and the elements bonded to siliceous material [1]. In this study, HF was used together with nitric acid and hydrochloric acid to digest aerosol filter samples for trace element analysis. Because of its high sensitivity, wide dynamic range and relatively low possibility of interferences as well as its multi-elemental characteristics, inductively coupled plasma mass spectrometry (ICP-MS) has been chosen as the analytical technique [2,3]. Although there are many advantages of ICP-MS, it suffers from both spectroscopic and non-spectroscopic interferences. However, mass spectral overlapping with polyatomic ions, has been recently overcome by the use of high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). High resolution ICP-MS relies on a magnetic sector to separate ions with greater discrimination according to their mass/charge ratio [4–6].

The performance of HR-ICP-MS technique has been evaluated in terms of uncertainties of the measurements in the determination of 35 elements in aerosol samples. Numerous papers referring to experimental studies on the metal contents in aerosol samples have been published, but none of them have calculated the estimation of measurement uncertainties. It is unavoidable to calculate the measurement uncertainties when the trace and ultra trace levels of elements are determined. For this reason, it is necessary to identify all the possible sources of uncertainties related to the analytical procedure.

2. Experimental

2.1. Sampling

Atmospheric particulate samples were collected between December 2005 and September 2006. Samples were collected by a dichotomous sampler (Andersen SA 241). The sampling place is located in the city center of Eskisehir. The urban atmosphere of Eskisehir is characterized by many sources like coal burning for residential heating and very high traffic. This sampler allows measuring coarse PM$_{(2.5-10)}$ and fine (PM$_{2.5}$) particles at the same time. Particles were collected on polytetrafluoroethylene (PTFE)

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Table 1
Operating conditions for the HR-ICP-MS.

Parameter	Value
RF power (W)	1230
Coolant gas flow (L min^{-1})	16
Auxiliary gas flow (L min^{-1})	0.8
Nebulizer	PFA micronebulizer (50 μL min^{-1})
Sample gas flow (L min^{-1})	1.18
Sampling cone (orifice dia., mm)	Platinum (1)
Skimmer cone (orifice dia., mm)	Platinum (0.8)
Injector	Sapphire
Peristaltic pump flow (rpm)	18
Spray chamber	PFA
Nominal resolution	LR = 400, MR = 4000, HR = 10,000
Scanning mode	Both (analog and counting)
Number of scans for each isotope	9 for each resolution
Sample time (ms)	10 (LR), 20 (MR), 50 (HR)
Ion lens setting	Adjusted to obtain maximum signal/noise ratio
Auto sampler	CETAC ASX-510
Rinse time (s)	20
Sample uptake time (s)	80

LR: Low resolution, MR: medium resolution, HR: high resolution.

filter (diameter 37 mm, pore size 2 μm, Andersen Instruments Inc., Smyrna, USA). The total sampling flow rate was 16.7 L min^{-1}. Totally 274 coarse samples and 274 fine samples were collected and analyzed. The coarse and the fine samples were collected at flow rates of 1.67 L min^{-1} and 15 L min^{-1}, respectively.

2.2. Instrumentation and operating parameters

The analyses were performed by using Thermo Finnigan Element 2 (Bremen, Germany) High Resolution ICP-MS instrument. The operating parameters are summarized in Table 1, the isotopes and the corresponding mass resolution modes used in the measurements are given in Table 2.

2.3. Preliminary sample preparation and handling

Before and after each sampling, the filters were conditioned to a constant weight in a cabinet type desiccator between 25 °C and 35 °C and relative humidity between 25% and 35% for more than 24 h and were handled in a way that all the risks of contamination as well as loss of sample were minimized. Blank filters were handled identically to the samples, but were run on the sampler of the collection instrument for 1 min which was the approximate time required to push the start button for real samples. Until the sampling time, the empty filter paper should be exposed to the same conditions with the filter paper on which samples were collected. Field blanks were taken once weekly. For the majority of the study period, 24-h samples were taken.

After collection of the samples, filter cassettes were delivered to the laboratory in precleaned petri dishes. Filters were removed from the cassettes by Teflon coated blades. Filters were weighed on an analytical balance (Sartorius CP124S) with a precision of 0.01 mg. Cutting the filter into half was necessary, since the second half was used for determination of ions. Each part of the filter was transferred into clean petri dish, labeled, sealed and stored in a dark cupboard until digestion and analysis.

Table 2
Isotopes and mass resolution of elements.

Isotopes	Mass resolution modes	Isotopes	Mass resolution modes
^{27}Al	LR, MR	^{23}Na	MR, HR
^{75}As	HR	^{143}Nd, ^{146}Nd	LR
^{197}Au	LR	^{62}Ni	MR
^{137}Ba, ^{135}Ba	LR, MR	^{31}P	MR
^{42}Ca, ^{43}Ca, ^{44}Ca	MR, HR	^{206}Pb, ^{208}Pb	LR, MR
^{111}Cd, ^{114}Cd	LR	^{121}Sb	LR
^{140}Ce	HR	^{45}Sc	MR
^{59}Co	MR	^{77}Se, ^{78}Se	HR
^{52}Cr, ^{53}Cr	MR	^{149}Sm, ^{152}Sm	LR
^{63}Cu, ^{65}Cu	LR, MR	^{118}Sn	LR, HR
^{151}Eu, ^{153}Eu	MR	^{86}Sr, ^{88}Sr	LR
^{56}Fe, ^{57}Fe	MR, HR	^{122}Te, ^{124}Te	MR
^{155}In*	All modes	^{46}Ti, ^{49}Ti	MR
^{39}K	HR	^{203}Tl, ^{205}Tl	LR
^{138}La, ^{139}La	LR	^{238}U	LR, MR
^{7}Li	LR	^{51}V	MR
^{55}Mn	LR, MR	^{182}W, ^{183}W	LR
^{95}Mo, ^{100}Mo	LR	^{66}Zn, ^{68}Zn	LR, MR

* ^{115}In is used as an internal standard.

2.4. Reagents

All reagents used in the analysis are analytical or higher grade. Suprapure nitric acid (65%, w/w), hydrochloric acid (30%, w/w) and analytical grade hydrofluoric acid (40%, w/w) were purchased from Merck (Germany). Deionized water obtained from Millipore MilliQ Academic water purification system with a resistivity of 18.2 MΩ was used throughout the experiments. The multi-element standard stock solutions were prepared from 100 μg mL^{-1} (High Purity, USA) mixture standards and/or 1000 μg mL^{-1} single element standard solutions (High Purity, USA). The intermediate standard solutions (1 μg mL^{-1}, 0.1 μg mL^{-1} and 0.01 μg mL^{-1}) used for the preparation of calibration standard solutions were prepared from 100 μg mL^{-1} stock mixture freshly.

2.5. Sample preparation and microwave digestion

The microwave (MW) digestion systems used for the decomposition and digestion of the samples collected on filter papers were a Milestone Ethos SEL (Sorisole, Italy) equipped with MPR 600/12 rotor and CEM MARS5 XP1500 system (Matthews, NC, USA). Half filter samples were placed into digestion vessels and 5 mL of nitric acid (65%, w/w), 1 mL of hydrochloric acid (30%, w/w) and 0.5 mL of hydrofluoric acid was added into the PTFE digestion vessels using Teflon coated forceps. After closing the vessels, they were subjected to a two-step microwave digestion program which was the same for both MW digestion systems. In the first step of the optimized digestion program, the maximum MW power was used and the temperature was increased from room temperature to 180 °C within 5 min. In the second step, the temperature was kept constant at 180 °C for 10 min. Then the digestion vessels were cooled down to room temperature before opening and transferring to volumetric flasks. The samples were diluted to 25 mL with deionized water using precleaned perfluoroalkoxy (PFA) volumetric flasks, which were calibrated and certified.

3. Results and discussion

3.1. Validation

An urban particulate matter standard reference material of SRM 1648 issued from National Institute of Standard and Technology (NIST, Gaithersberg, MD, USA), the reagent blanks and the standard solutions were used to validate the present analytical method.

3.1.1. Linearity

Standard addition methods were used for all calibrations. For the preparation of standard solutions, a representative mixture of sample matrix for a set of sample digests to be analyzed was prepared by mixing at least 10–15 sample digests from the same sample set.

Table 3
Linear range, LOD and LOQ.

Elements	Linear* range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)	Elements	Linear* range ($\mu g\,L^{-1}$)	LOD ($\mu g\,L^{-1}$)	LOQ ($\mu g\,L^{-1}$)
Al	0–500	10	33	Na	0–500	22	73
As	0–40	0.4	1.3	Nd	0–40	0.04	0.013
Au	0–40	0.9	3.0	Ni	0–40	3.4	11
Ba	0–500	0.6	2.0	P	0–500	4.9	16
Ca	0–500	54	180	Pb	0–40	0.34	1.1
Cd	0–40	0.08	0.26	Sb	0–40	0.15	0.50
Ce	0–40	0.43	1.4	Sc	0–40	0.045	0.15
Co	0–40	0.29	0.98	Se	0–40	1.0	3.4
Cr	0–500	1.1	3.7	Sm	0–40	0.022	0.074
Cu	0–500	1.9	6.4	Sn	0–40	0.58	1.9
Eu	0–40	0.004	0.015	Sr	0–40	0.58	1.9
Fe	0–500	53	177	Te	0–40	0.61	2.0
K	0–40	8	25	Ti	0–40	2.6	8.7
La	0–40	0.011	0.037	Tl	0–40	0.009	0.030
Li	0–40	0.18	0.61	U	0–40	0.010	0.033
Mn	0–500	1.5	5.1	V	0–40	0.048	0.16
Mo	0–40	0.12	0.39	W	0–40	0.030	0.10
				Zn	0–500	30	100

* Values represent the concentration of standard spiked into sample matrix.

For the determination of major elements the standards were prepared in 1:5 diluted sample matrices. In the determination of minor and trace constituents, the sample matrix solution was diluted only by the standards and the internal standard solution addition; the dilution ratio was only 4.975:5.

The determination of major and minor constituents was performed by using two different measurement methods. Some of the elements were included in both measurement methods in order to perform cross check. The range of the concentration of the elements in the calibration solutions were determined according to their expected concentration values in the sample digests and kept wide so that the measured intensities felt into the linear range. Consequently, the calibration curves for minor and trace elements (As, Au, Cd, Ce, Co, Eu, K, La, Li, Mo, Nd, Ni, Pb, Sb, Sc, Se, Sm, Sn, Sr, Te, Ti, Tl, U, V, W) were ranged from matrix solution concentration to an added concentration of 500 $\mu g\,L^{-1}$ (Table 3) and those for majors (Al, Ba, Ca, Cr, Cu, Fe, Mn, Na, P, Zn) were ranged from matrix solution concentration to 40 $\mu g\,L^{-1}$ (Table 3). The concentration of In which was used as an internal standard was 10 $\mu g\,L^{-1}$ in all solutions including standards and the samples as well as the blanks. The calibration lines for all the isotopes monitored had a correlation coefficient of at least 0.999 or better.

3.1.2. *LOD and LOQ*

The limit of detection was estimated as the concentration corresponding to three times the standard deviation (3σ) of the blank signals obtained from a set of reagent blanks (n = 45–50). The limit of detection (LOD) and the limit of quantification (LOQ, ten times) for the elements determined are shown in Table 3. The detection limits for all the elements investigated were found to be in the range of 0.004 $\mu g\,L^{-1}$ and 54 $\mu g\,L^{-1}$.

3.1.3. *Recovery and precision*

In order to evaluate the accuracy of the complete method including digestion and the measurements, SRM 1648, urban dust (NIST, Gaithersberg, MD, USA), certified reference material (CRM) was analyzed together with the samples applying the same digestion and measurement procedure. Each set of sample digestion

Table 4
Percent recovery for each element found in NIST SRM 1648, urban dust.

Element	Number of analysis	Found concentration ($\mu g\,g^{-1}$)	Certified value ± U (k = 2) ($\mu g\,g^{-1}$)	Recovery (%) ± %RSD
Al	46	36040	34200 ± 1100	105 ± 3.82
As	40	130	115 ± 10	114 ± 4.04
Ba	42	795	737*	108 ± 4.24
Cd	46	81	75 ± 7	108 ± 5.33
Ce	48	51	55*	93 ± 12
Co	47	19	18*	104 ± 3.89
Cr	42	320	403 ± 12	79 ± 18
Cu	44	680	609 ± 27	112 ± 6.93
Eu	48	0.83	0.8*	104 ± 6.62
Fe	46	42900	39100 ± 1000	110 ± 10.9
K	43	11530	10500 ± 100	110 ± 6.96
La	48	38	42*	91 ± 11
Mn	43	870	786 ± 17	111 ± 3.59
Na	39	4910	4250 ± 20	116 ± 4.29
Ni	45	106	82 ± 3	129 ± 7.89
Pb	46	6490	6550 ± 80	99 ± 4.07
Sb	42	47	45*	105 ± 9.97
Sc	48	7.0	7*	100 ± 6.31
Se	45	29	27 ± 1	108 ± 17.4
Sm	48	4.6	4.4*	105 ± 2.96
Ti	48	4050	4000	101 ± 6.14
U	48	5.8	5.5 ± 0.1	106 ± 9.75
V	44	138	127 ± 7	109 ± 3.90
Zn	46	5040	4760 ± 140	106 ± 4.51

* Uncertified values.

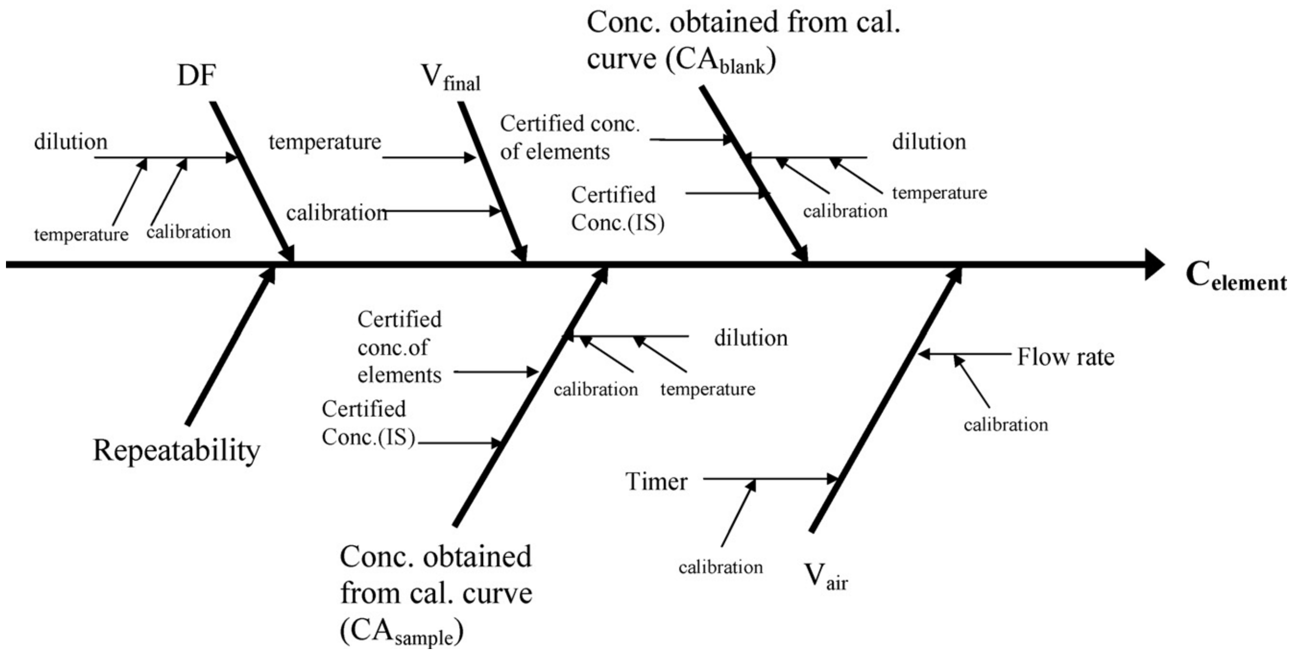

Fig. 1. Cause and effect diagram for the determination of elements in particulate samples.

contained one CRM (0.08–0.1 g) which is measured together with the same sample set. Reagent blank values were subtracted from the sample values in the calculation of recovery values. Recovery values for the elements whose values were certified in the CRM are shown in Table 4. The calculated percent recovery values varied between 79% and 129%. The highest recovery value belonged to Ni. Most of the values (90–110%) are consistent with other studies [7] that have found the recoveries of elements (Al, As, Cd, Cu, Fe, K, Ni, Pb, Se, U, V and Zn) changing between 80% and 98%. The low recovery of Cr in this SRM is a documented problem [3,8]. It has been hypothesized that the high soot content of NIST SRM 1648 signifies the presence of organic material that somehow inhibits dissolution of all chromium [7]. The %RSD values were taken into account for long-term variations. Each sample was prepared in different days during the analysis period of approximately one year. Therefore, %RSD values were ranged between 2.96% and 18% for the measured elements in this study.

3.2. Estimation of uncertainty

3.2.1. Identification of uncertainty sources

The element concentrations in the filter samples expressed in ng $\mathrm{m^{-3}}$, were calculated by using Eq. (1):

$$\text{Concentration} = \frac{(\mathrm{CA_{sample}} - \mathrm{CA_{reagentblank}}) \times V_{\mathrm{final}}}{V_{\mathrm{air}}} \times \mathrm{DF} \qquad (1)$$

where $\mathrm{CA_{sample}}$ is the element concentration in the sample obtained from the calibration (ng $\mathrm{mL^{-1}}$); $\mathrm{CA_{reagentblank}}$ is the element concentration in the reagent blank obtained from the calibration (ng $\mathrm{mL^{-1}}$); V_{final} is the final diluted volume (25 mL) after the digestion; V_{air} is the volume of air for the sample; DF is the dilution factor (samples are diluted before the analysis).

Table 5
Volumetric material used for preparing standards.

Equipment	Uncertainty (mL)	Variation coefficient (%)
Volumetric flask 100 mL	±0.014	
Volumetric flask 25 mL	±0.008	
Automatic pipette 0.5–5 mL		0.08
Automatic pipette 100–1000 μL		0.23
Automatic pipette 10–100 μL		0.18

3.2.2. Identification of standard uncertainties associated with each step

For the identification of the uncertainty sources, the use of cause and effect diagram is drawn (Fig. 1). The diagram is helpful to prevent an uncertainty contribution incorporated into the budget more than once. Furthermore, it is possible to decide which sources are more significant than the others and which ones are negligible. As can be seen from the figure, the main parameters that affect the concentration of the elements were the volume of air, the concentrations that were obtained from the calibration curve, final volume of sample digested, dilution factors and repeatability. Therefore, the following parameters were involved in the calculation of the concentrations of the elements in the samples collected on PTFE filters:

1. Calibration curves, stock solutions of standards and internal standard (CA)
2. Final volume of the sample digested (V_{final})
3. Volume of air withdrawn by the dichotomous sampler (V_{air})

Table 6
Calculation of relative uncertainty (%) for As in a fine particulate sample.

Parameter	Value (X)	$u(X)$	$u(X)/X$
Stock solution (1 mg $\mathrm{L^{-1}}$)	1	0.005	0.005
Stock solution (100 μg $\mathrm{L^{-1}}$)	0.1	0.0006	0.006
Stock solution (10 μg $\mathrm{L^{-1}}$)	0.01	0.000063	0.0063
IS stock solution (1 mg $\mathrm{L^{-1}}$)	1.0	0.00240	0.0024
Sample volume (mL)	25	0.0121	0.0005
Sample dilution	1.0	0.0051	0.0051
Calibration uncertainty	1.0	0.029	0.029
Repeatability	100	0.64	0.0064
Volume of air	21.6	0.13	0.0062
Relative combined uncertainty			0.0323
Measurement result (ng $\mathrm{m^{-3}}$)	0.25		
Standard combined uncertainty		0.0081	
Expanded uncertainty (k = 2)		0.016	
Relative uncertainty (%)		6.46	

Table 7
The relative expanded uncertainties of all elements for coarse and fine sample.

Elements	Expanded relative uncertainty for coarse samples	Expanded relative uncertainty for fine samples	Elements	Expanded relative uncertainty for coarse samples	Expanded relative uncertainty for fine samples
Al	4.1	2.9	Na	9.4	9.0
As	7.0	6.5	Nd	5.1	4.2
Au	17	16	Ni	7.4	6.8
Ba	7.8	7.2	P	5.5	4.6
Ca	4.8	3.8	Pb	6.7	6.0
Cd	5.0	4.5	Sb	7.7	7.1
Ce	7.5	6.8	Sc	7.3	6.6
Co	5.5	4.6	Se	8.7	8.2
Cr	15	14	Sm	5.1	4.1
Cu	4.6	3.5	Sn	9.0	8.5
Eu	5.3	4.4	Sr	5.9	5.1
Fe	8.9	8.4	Te	5.9	5.1
K	11	11	Ti	5.6	4.8
La	5.9	5.1	Tl	18	18
Li	6.0	5.2	U	5.5	4.6
Mn	6.8	6.1	V	4.6	3.5
Mo	5.3	4.4	W	5.6	4.8
			Zn	4.5	3.4

4. Repeatability
5. Dilution factor (DF)

Thus the uncertainty in the concentrations is a combination of the uncertainties of each of the above mentioned parameters. The combined uncertainty (in terms of relative uncertainty) can be calculated by using Eq. (2):

$$u_{rel}(C)=\sqrt{u_{rel}^{2}(\mathrm{CA})+u_{rel}^{2}(V_{\mathrm{final}})+u_{rel}^{2}(V_{\mathrm{air}})+u_{rel}^{2}(rep)+u_{rel}^{2}(\mathrm{DF})} \tag{2}$$

3.2.2.1. Estimation of the uncertainty derived from the dilution of the sample extract, u(V_{final}) and dilution factor u(DF). After the decomposition procedure the samples were diluted to 25 mL with deionized water. Then, from this solution 4.975 mL was taken using 5 mL micropipette and 25 μL IS was added using 100 μL automatic micropipette in such a way that the standards were prepared for the determination of minor elements. Before the measurements for the major constituents, 2 mL was taken from the sample digests using 5 mL automatic pipette and 8 mL deionized water was added using 5 mL automatic pipette in two steps. These solutions were prepared in precleaned 10-mL polyethylene vial.

Table 8
Percent contribution of each effect to the total uncertainty for coarse particles.

Elements	Stock sol. ($1\,\mathrm{mg\,L^{-1}}$)	Stock sol. ($100\,\mathrm{\mu g\,L^{-1}}$)	Stock sol. ($10\,\mathrm{\mu g\,L^{-1}}$)	IS stock sol. ($1\,\mathrm{mg\,L^{-1}}$)	Sample volume (mL)	Sample dilution	Cal.	Repeat.	Vol. of air
Al	10	12	13	5.0	1.0	11	2.3	12	34
As	6.5	7.8	8.2	3.1	0.6	6.6	38	8.4	21
Au	3.3	4.0	4.1	1.4	0.2	10	17	50	11
Ba	6.2	7.4	7.7	3.0	0.6	6.2	41	8.1	20
Ca	8.3	9.9	10	4.0	0.8	8.4	18	13	27
Cd	7.5	8.9	9.4	3.1	0.5	23	12	12	24
Ce	5.5	6.6	6.9	2.3	0.4	17	25	19	18
Co	7.4	8.8	9.3	3.0	0.5	23	16	8.4	24
Cr	3.7	4.4	4.6	1.8	0.4	3.8	48	21	12
Cu	8.9	11	11	4.3	0.9	9.0	7.9	19	29
Eu	7.9	9.4	9.8	3.2	0.5	24	4.7	15	25
Fe	5.3	6.4	6.7	2.6	0.5	5.4	39	17	17
K	4.6	5.5	5.7	1.9	0.3	14	44	9.7	15
La	7.1	8.4	8.8	2.9	0.5	22	5.1	23	23
Li	6.7	8.0	8.4	2.8	0.4	21	12	19	22
Mn	6.8	8.1	8.4	3.2	0.7	6.8	37	7.4	22
Mo	7.7	9.2	9.6	3.2	0.5	23	7.2	14	25
Na	5.5	6.6	6.9	2.7	0.5	5.6	47	7.6	18
Nd	8.1	9.7	10	3.3	0.5	25	5.6	11	26
Ni	5.7	6.8	7.1	2.3	0.4	17	29	13	18
P	7.9	9.4	9.8	3.8	0.8	7.9	29	6.0	25
Pb	6.8	8.1	8.5	3.3	0.7	6.9	36	8.1	22
Sb	5.5	6.5	6.8	2.2	0.3	17	27	17	18
Sc	5.9	7.0	7.3	2.4	0.4	18	30	11	19
Se	4.9	5.8	6.1	2.0	0.3	15	25	25	16
Sm	8.2	9.8	10	4.0	0.8	8.3	25	7.0	27
Sn	5.3	6.3	6.6	2.5	0.5	5.3	38	19	17
Sr	7.3	8.6	9.1	3.5	0.7	7.3	30	9.7	23
Te	7.2	8.6	9.0	3.4	0.7	7.2	12	29	23
Ti	7.3	8.7	9.2	3.5	0.7	7.4	27	13	24
Tl	3.7	4.4	4.6	1.8	0.4	3.7	3.7	66	12
U	7.3	8.7	9.1	3.5	0.7	7.4	19	21	24
V	8.8	11	11	4.2	0.9	8.9	17	10	28
W	7.2	8.6	9.0	3.5	0.7	7.3	24	17	23
Zn	8.8	10	11	4.2	0.9	8.9	16	12	28

The temperature effect describes the dispersion produced by a variation of liquid temperature through a rectangular distribution [9] within ±3 °C around the calibration temperature.

$$u_{\text{vtemp}} = \frac{3 \times V \times Q}{1.73} \tag{3}$$

where u_{vtemp} represents the standard uncertainty of the temperature effect, V is the measured volume (e.g. 25 mL) and Q is the coefficient of volume expansion of the water ($Q_{\text{water}} = 0.000124\,^{\circ}\text{C}^{-1}$). The volumetric calibration standard uncertainty, $u_{\text{vcal,}}$ of 5 mL automatic pipette, u_{vcal} is calculated from the manufacturer reported CV value of 0.1 (i.e. $u_{\text{vcal}} = (0.1/100) \times 5 = 0.005$ mL). The volumetric standard uncertainty of 100 μL automatic pipette was calculated in the same manner. These values are combined in Eq. (4) to calculate the uncertainty arising from the dilution of the samples solutions.

These sources are combined in Eq. (4):

$$u_{\text{v}} = \sqrt{(u_{\text{vcal}})^2 + (u_{\text{vtemp}})^2} \tag{4}$$

Another source of uncertainty arising from the sample dilution is the repeatability. However, it is not included here since the repeatability for all possible sources is collected under repeatability term separately. Uncertainties of volumetric flasks and automatic pipettes were calculated using the values given in Table 5.

3.2.2.2. Estimation of the uncertainty derived from the estimation of the calibration curves, stock solutions of standards and internal standard, u(CA). This term is a combination of the uncertainties associated with the preparation of the stock solutions and the calibration curve and given in Eq. (5). The uncertainty of the preparation of stock solutions (1 mg L^{-1}, 0.1 mg L^{-1} and 0.01 mg L^{-1}) is also a combination of uncertainty of elemental concentrations given in the certificate by the manufacturer, u_{element}, and uncertainty coming from the volumetric flasks and pipettes used for dilution, u_{v} (Table 4). The uncertainties of calibration standards are given as 100 ± 0.05 mg L^{-1} for each element. Eq. (4) was used to calculate the uncertainty coming from the volumetric flasks as well as the micropipettes.

$$u_{\text{std}} = \sqrt{(u_{\text{v}}/V)^2 + (u_{\text{element}}/C_{\text{element}})^2} \times C_{\text{std}} \tag{5}$$

where C_{element} is the concentration of element in main stock solution (100 mg L^{-1}); C_{std} is the concentration of intermediate standard solutions (1 mg L^{-1}, 0.1 mg L^{-1} and 0.01 mg L^{-1}).

The internal standard stock solution (In) was prepared from 1000 ± 3 mg L^{-1} main solution. The 0.1 mL was taken from this stock solution and diluted to 100 mL to prepare 1 mg L^{-1} In internal standard solution.

The uncertainty associated with the calibration curve is calculated by using the formula given in EURACHEM/CITAC guide [9]. The six calibration standarts were prepared and the instrument was run to acquire 9 replicate measurements from each solution.

3.2.2.3. Estimation of the repeatability uncertainty, u(rep.). The uncertainty from the repeatability covers the contributions from purity of acids, losses from digestion procedure, accuracy of calibration, stability of the instrument, etc. Whole procedures were applied to five subsamples and their results were used in the calculation of uncertainty arising from repeatability term. The

Table 9
Percent contribution of each effect to the total uncertainty for fine particles.

Elements	Stock sol. (1 mg L^{-1})	Stock sol. (100 μg L^{-1})	Stock sol. (10 μg L^{-1})	IS stock sol. (1 mg L^{-1})	Sample volume (mL)	Sample dilution	Cal.	Repeat.	Vol. of air
Al	13	16	16	6.3	1.3	13	2.9	15	16
As	7.5	9.0	9.4	3.6	0.7	7.6	43	9.6	9.4
Au	3.5	4.2	4.4	1.5	0.2	11	18	53	4.4
Ba	7.0	8.4	8.8	3.4	0.7	7.1	47	9.2	8.8
Ca	9.9	12	12	4.8	1.0	10	22	16	12
Cd	8.8	11	11	3.6	0.6	27	14	14	11
Ce	6.2	7.4	7.8	2.6	0.4	19	28	21	7.8
Co	8.7	10	11	3.6	0.6	27	19	9.9	11
Cr	4.0	4.8	5.0	1.9	0.4	4.0	52	23	5.0
Cu	11	13	14	5.2	1.0	11	9.6	23	13
Eu	9.3	11	12	3.8	0.6	28	5.5	18	12
Fe	6.0	7.1	7.4	2.9	0.6	6.0	43	19	7.4
K	5.0	6.0	6.3	2.1	0.3	15	48	11	6.3
La	8.2	9.8	10	3.4	0.5	25	6.0	26	10
Li	7.7	9.2	9.7	3.2	0.5	24	14	22	9.7
Mn	7.8	9.3	9.8	3.7	0.8	7.9	42	8.5	9.7
Mo	9.1	11	11	3.7	0.6	28	8.6	17	11
Na	6.2	7.4	7.8	3.0	0.6	6.3	52	8.5	7.8
Nd	9.7	12	12	4.0	0.6	30	6.7	14	12
Ni	6.4	7.6	8.0	2.6	0.4	20	32	15	8.0
P	9.3	11	12	4.5	0.9	9.4	35	7.1	12
Pb	7.9	9.4	9.8	3.8	0.8	7.9	41	9.4	9.8
Sb	6.1	7.3	7.6	2.5	0.4	19	31	19	7.6
Sc	6.6	7.9	8.3	2.7	0.4	20	33	12	8.3
Se	5.4	6.5	6.8	2.2	0.3	17	27	28	6.8
Sm	9.8	12	12	4.7	1.0	10	30	8.4	12
Sn	5.9	7.0	7.3	2.8	0.6	5.9	42	21	7.3
Sr	8.5	10	11	4.1	0.8	8.6	36	11	11
Te	8.4	10	10	4.0	0.8	8.4	14	34	10
Ti	8.6	10	11	4.1	0.8	8.7	31	15	11
Tl	4.0	4.7	5.0	1.9	0.4	4.0	4.0	71	5.0
U	8.6	10	11	4.1	0.8	8.7	22	24	11
V	11	13	13	5.1	1.0	11	20	13	13
W	8.4	10	11	4.0	0.8	8.5	28	20	11
Zn	11	13	13	5.1	1.0	11	19	14	13

Table 10
Statistical overview of analyzed coarse samples (ng m^{-3}).

Elements	N	Quantification (%)	Arithmetic average	Median	Geometric mean	Standard deviation	Min.	Max.
Al	222	84	8700	7010	6550	6010	240	29330
As	250	96	29	23	19	29	0.04	247
Au	221	84	6.4	3.4	2.7	9.3	0.004	80
Ba	264	100	133	114	105	86	2	526
Ca	264	100	24400	17950	16930	19130	550	108100
Cd	264	100	8.1	6.3	5.9	6.4	0.1	49.5
Ce	262	99	12	10	9.7	9.3	0.4	92
Co	247	94	7.0	5.8	5.5	4.6	0.1	30
Cr	256	97	70	60	58	39	1	200
Cu	261	99	176	147	140	120	3	720
Eu	182	69	0.10	0.06	0.05	0.14	0.0005	1.10
Fe	239	91	6415	5090	4980	4390	145	26120
K	264	100	4379	3774	3548	2903	75	25640
La	255	97	5.8	4.7	4.4	4.6	0.1	41
Li	264	100	8.5	6.3	6.6	6.9	0.2	52
Mn	263	100	153	123	117	104	1	590
Mo	263	100	9.2	7.1	7.1	7.5	0.03	61
Na	232	88	2910	2530	2310	1980	54	11420
Nd	263	100	3.7	2.8	2.7	3.6	0.03	36
Ni	263	100	95	74	73	75	6	390
P	264	100	516	406	393	443	6	3001
Pb	264	100	337	277	250	258	3	2200
Sb	248	94	30	23	23	23	0.1	190
Sc	257	97	1.8	1.3	1.2	1.5	0.01	12
Se	179	68	12	9.4	7.5	9.3	0.04	46
Sm	263	100	0.68	0.47	0.46	0.67	0.000014	5.9
Sn	264	100	36	26	26	53	1.9	770
Sr	240	91	62	49	48	41	0.09	240
Te	264	100	33	24	24	49	1.7	700
Ti	251	95	540	430	410	430	16	3985
Tl	260	98	2.2	1.8	1.6	1.9	0.01	13
U	248	94	0.74	0.62	0.59	0.45	0.001	2.8
V	264	100	53	38	37	47	0.2	320
W	264	100	4.6	2.3	2.5	6.1	0.06	50
Zn	262	99	1740	1200	1230	1510	24	8360

%RSD of the concentrations of the elements calculated for CRM digests which were prepared and analyzed on different days was calculated. The standard deviation of the repeatability data mentioned above represented the repeatability standard uncertainty. To achieve the standard uncertainty, mean %RSD of these samples was divided by the square root of the number of samples, *n*, $(\mathrm{RSD}/\sqrt{n})$.

3.2.2.4. Estimation of the uncertainty derived from volume of air withdrawn by the dichotomous sampler, (u_{vair}). In the dichotomous air sampler manual, the accuracy of all flow measurements was given as ±1.5%. In the determination of air volume passed during the sampling period is calculated by using Eq. (6):

$$V_{\mathrm{air}} = F \times t \tag{6}$$

where *F* is the flow of air ($\mathrm{m}^3\,\mathrm{min}^{-1}$); *t* is the sampling period (usually 24 h). The accuracy of timer is given as ±15 min in 24 h. The ideal flow of air passed from coarse filter is 0.00167 $\mathrm{m}^3\,\mathrm{min}^{-1}$ and the ideal flow of air passed from fine filter is 0.015 $\mathrm{m}^3\,\mathrm{min}^{-1}$ (without considerable pressure drop). The standard uncertainty of coarse flow, u_{flow}, is calculated from the manufacturer value (i.e. $u_{\mathrm{flow}} = (1.5 \times 0.00167/100) = 2.5 \times 10^{-5}\,\mathrm{m}^3\,\mathrm{min}^{-1}$). The standard uncertainty of time for 24 h period, u_{time}, is calculated as 15/1.73 = 8.7 min assuming a rectangular distribution. The same formula is applied for the calculation of uncertainty in sampling period for fine samples. The standard uncertainty of volume of air is calculated using Eq. (7):

$$u_{\mathrm{vair}} = \sqrt{(u_{\mathrm{v}}/V_{\mathrm{air}})^2 + (u_{\mathrm{time}}/\mathrm{time})^2} \times V_{\mathrm{air}} \tag{7}$$

where V_{air} (coarse) is 2.41 m^3; V_{air} (fine) is 21.6 m^3 for 24 h sampling period.

3.3. Estimation of expanded uncertainties

As an example, the calculation of relative uncertainty for element As was given in Table 6. The relative expanded uncertainties were calculated for all elements and the results were tabulated in Table 7. The percent contribution of each source to the relative combined uncertainties is given in Tables 8 and 9. It might be seen that the contribution from the calibration curve, repeatability and volume of air (Fig. 1) were the major sources. The uncertainties coming from the preparation of stock solutions (contributes to the concentration obtained from the calibration curve, CA, in the fishbone diagram), dilution after digestion and dilution required for the analysis did not contribute very much to the relative combined uncertainties.

3.4. Analysis of real samples

The real samples were analyzed using the conditions discussed above. The data obtained by coarse (Table 10) and fine (Table 11) samples were statistically evaluated. Percentages of quantification are given in the third column of the tables. The following columns involve the data of arithmetic mean, median, geometric mean, standard deviation, minimum and maximum values. Only some elements were not quantified in all analyzed samples. The concentrations of elements Eu and Se were quantified only in 69% and 68% of the coarse samples, respectively. Aluminum and Au were determined quantitatively in 84% of the coarse samples. Other elements were detected in more than 90% of the samples. In fine samples,

Table 11
Statistical overview of analyzed fine samples (ng m^{-3}).

Elements	*N*	Quantification (%)	Arithmetic average	Median	Geometric mean	Standard deviation	Min.	Max.
Al	239	92	600	140	170	1650	5	18100
As	197	75	0.54	0.36	0.32	0.65	0.009	5.1
Au	193	74	0.65	0.36	0.29	0.86	0.006	6.3
Ba	260	100	2.1	0.9	0.9	3.6	0.03	25
Ca	205	79	350	180	160	670	0.5	7690
Cd	250	96	0.13	0.10	0.092	0.12	0.0036	0.84
Ce	220	85	0.29	0.12	0.12	0.52	0.00056	3.8
Co	196	75	0.25	0.15	0.14	0.31	0.0011	2.5
Cr	233	89	2.3	1.7	1.6	2.2	0.039	14
Cu	257	98	3.4	2.4	2.2	3.2	0.08	19
Eu	135	60	0.01299	0.0098	0.0088	0.010	0.0012	0.039
Fe	205	79	140	72	66	250	0.29	2500
K	257	98	71	42	46	96	6.5	860
La	246	94	0.092	0.030	0.031	0.23	0.0010	2.1
Li	254	97	0.20	0.076	0.084	0.39	0.0014	3.0
Mn	242	93	1.8	1.1	1.1	2.7	0.14	25
Mo	250	96	0.26	0.11	0.11	0.44	0.0032	3.5
Na	229	88	88	51	48	130	0.059	1280
Nd	234	90	0.070	0.016	0.018	0.18	0.00050	1.4
Ni	238	91	3.4	1.7	1.9	4.3	0.04	31
P	261	100	20	6.6	7.4	38	0.10	260
Pb	245	94	3.9	2.8	2.8	3.6	0.23	23
Sb	240	92	0.37	0.26	0.24	0.49	0.014	4.5
Sc	254	97	0.028	0.0082	0.0084	0.067	0.00013	0.51
Se	184	71	28	2.6	3.2	86	0.025	860
Sm	214	83	0.0089	0.0030	0.0034	0.023	0.00010	0.18
Sn	259	99	1.32	0.69	0.66	2.4	0.0094	24
Sr	251	96	1.24	0.51	0.50	2.0	0.0061	17
Te	260	100	1.20	0.61	0.60	2.2	0.0071	21
Ti	236	90	10	6.9	6.6	13	0.49	120
Tl	255	98	0.033	0.021	0.020	0.038	0.0014	0.29
U	248	95	0.033	0.0063	0.0060	0.12	0.00004	1.1
V	240	92	0.54	0.39	0.38	0.54	0.047	3.8
W	254	97	0.16	0.069	0.063	0.33	0.00075	3.5
Zn	254	97	69	29	31	94	0.42	560

Eu was found in only 60% of the samples. The elements Se, Au, Co, Ca, Fe and Sm were quantified in the range of 71% and 83%. Other elements were found in more than 85% of the samples.

4. Conclusions

The present method is based on microwave acid digestion of aerosol samples collected on PTFE filters, which allow the simultaneous determination of 35 elements, by High Resolution ICP-MS. It showed satisfactory validation parameters such as accuracy, precision, lower detection limits and selectivity.

In the literature there are no data for calculation of measurement and sampling uncertainty for the determination of elements in air samples even though there are some studies related with method validation. Relative expanded uncertainties for each element using coverage factor 2 were between 2.9% and 18%.

The validated method was used to analyze 274 coarse and 274 fine air samples. Thanks to the properties of high sensitivity and high resolution of HR-ICP-MS instrument, the very large and important data sets were obtained to determine the atmospheric pollution levels in Eskisehir. The methods can easily be extended to other matrices.

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