

Assessment of a procedure to determine trace and major elements in atmospheric aerosol

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The determination of trace elements in atmospheric particulate is affected by a number of problems that arise from some critical points such as the blank of the filters, sample heterogeneity and pre-analytical treatments. In the framework of a monitoring campaign conducted in the Venice Lagoon the analytical methodology for the determination of 20 trace elements (Al, As, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, V, Zn) in atmospheric particulate samples by inductively coupled plasma quadrupole mass spectroscopy (ICP-QMS) has been optimized taking into account the individual critical points. Tests were carried out to estimate the blank contributions, and minimize the detection limit (LOD), measurements were also carried out to evaluate the accuracy and the repeatability. To obtain a complete dissolution of aerosol dust material and good recoveries of the elements, the acid mixture and the microwave assisted digestion program were optimized. The blank contributions from membrane filter manipulation and transportation prior to exposure were tested for the slotted and back filters by placing them on the sampling device for some minutes without air flowing to obtain field blanks (FBs). The contribution to the blank values of passive deposition and by contact with the samplers (quoted as campaign blanks, CBs) was measured by exposing the membranes throughout the sampling session (fifteen days) without any air flow. Instrumental ICP-QMS parameters were optimized and calibration curve intervals were selected on the basis of the necessity of simultaneous determination of the elements present at different levels of concentration. The limits of detection for each elements and the investigated method were suitable to determine the 20 elements reported above in the atmospheric aerosol fractionated in 6 classes ranging between 10 to 0.49 μm . It allows the determination of trace elements in aerosol in a large range of concentrations that can be observed in areas characterized by remarkable variability and regions with different levels of contamination.

Introduction

In the last few years much attention has been given to the evaluation of the elemental content of airborne particulate matter due their detrimental effects on human health. Many epidemiological studies have revealed that the degree of adverse respiratory effects depends on the physical and chemical properties of atmospheric aerosol.¹⁻³ The particulate matter with an aerodynamic diameter $<10 \mu\text{m}$ (PM10) constitutes the inhalable fraction of aerosol while the particulate matter with an aerodynamic diameter $<2.5 \mu\text{m}$ (PM2.5) could have more serious toxic effects as it constitutes the respirable fraction of the aerosol. Under this framework, European Commission (EC) legislation requires that member states monitor the PM10 and the lead concentration in atmosphere.⁴ Furthermore the EC has recently proposed the monitoring of other toxic elements such as arsenic, cadmium and nickel in atmospheric particulate.⁵

Since the atmospheric particulate samples are often constituted of minute quantities of dust (fractions of milligrams) collected onto large cellulose filters, as such total sample digestion is widely used for trace element analysis. Various methods using microwave-assisted digestion with different acid mixtures and different heating programs are described in the literature.⁶⁻⁹ Yet in the total digestion of aerosol samples, elements contained as impurities in the cellulose material as well as the large amounts of chemicals required could give high blank levels and matrix effects during analysis. Therefore a careful quality control and optimisation of the analytical procedure is indispensable.

The objectives of the present study were to develop a suitable methodology for sampling and for the quantitative determination of trace elements in atmospheric particulate with an accurate blank control, adequate detection limits, recoveries, accuracy and repeatability. The analytical methodology was then used to study the PM10 composition in relation to the content of Al, As, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, V and Zn in the aerosol of some sites of the Venice area with different anthropic influences.

Because of the significant differences between the local sources, we expect a large variability for elements at the trace level;

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therefore the analytical methodology will be used to detect an extended interval of concentrations.

Materials and methods

Size-fractionated PM₁₀ aerosol samples were collected by brushless high volume samplers (Tisch Environmental Inc., Village of Cleves, Ohio, USA) equipped with a six-stage cascade impactor separating particles in the following dimensional aerodynamic defined classes: 10–7.2 mm, 7.2–3 mm, 3–1.5 mm, 1.5–0.95 mm, 0.95–0.49 mm, <0.49 mm. Slotted cellulose filters (14 × 15 cm) were used to collect the first five fractions and a cellulose filter paper (Whatman grade 41, 20 × 25 cm) was used as a back filter at the end of impactor outlet to inertially collect particles of size <0.49 mm, the operating flow was 1.13 m³ min⁻¹.

Aerosol sampling was carried out over four campaigns from March 2002 to June 2003 at four sites in the Venice area. Sampling sites, as well wind direction and speed were chosen in order to evaluate the composition of the inorganic pollutants in areas affected by different sources (Fig 1). Marine and “long range” sources were monitored at site 2.

(“P. Sabbioni” station, lat. 45°25'21.8" N, long. 12°26'12.2" E), located on the Northern inlet of the lagoon on the light tower when winds were blowing from the south-east. Aerosol from urban and industrial sources were collected at site 1 (“Moranzani” station, lat. 45°25'38.5" N, long. 12°12'47.6" E) located south of the Mestre urban area and the Porto Marghera industrial area at site 4 (“Tessera” station, lat. 45°29'37.9" N, long. 12°19'27.2" E), located close the Venice Airport when winds were blowing from north-east. Aerosol less affected by local sources was sampled at site 3 located on Monte Grande in the Euganei Hills, a wooded area at 460 m above sea level and 50 Km from Venice (“Teolo” station, lat. 45°21'43.0" N long.

11°40'22.4" E), when wind blew from the north-east. For all the sites aerosol samples were taken when winds blew at a speed greater than 1 m s⁻¹. The sampling time was variable as a function of meteorological characteristics, therefore the gathered volume of each sample was changeable, it ranged between 500 m³ to 12000 m³.

Filter and vessels cleaning

All the analytical procedures (cleaning of filters and all plastic items, filter weighing, sample treatment, preparation of standard solutions) were performed under a laminar flow clean area in a class 100 clean chemistry laboratory. Ultrapure water was obtained from a purification system (PURELAB ULTRA from Elga Labwater/VWS - UK Ltd) and suprapure grade reagents (HCl and HNO₃ Merck) were used for all cleaning procedures.

Preliminary analysis carried out on untreated filters showed an extremely variable trace metal content, e.g. the content (SD) in µg/filter of Al, Ca Cd, Cu, V and Zn were 8(3), 23(21), 0.071(0.004), 0.20(0.04), 2.3(0.1) and 2.0(1.8) respectively. Therefore the filters before use were washed by HCl suprapure grade diluted 1:100 by ultrapure water and rinsed with ultrapure water, the procedure was repeated then the membranes were dried at room temperature in a class 100 laminar flow area. The procedure reduced the content for some elements of about one order of magnitude and overall increase significantly the repeatability of blank measurement. All filters were conditioned for 24 h at a temperature of 20° ± 5 °C and a relative humidity of 30 ± 5% and were then weighed by a balance with 0.01 mg precision (CP225D Sartorius). Filter weighings were repeated at least three times to assess aerosol masses ≥ 5 mg with a standard deviation of 5–10%. The slotted filters were cut into 4 equal sections and the backup filters were cut into 6 equal sections,

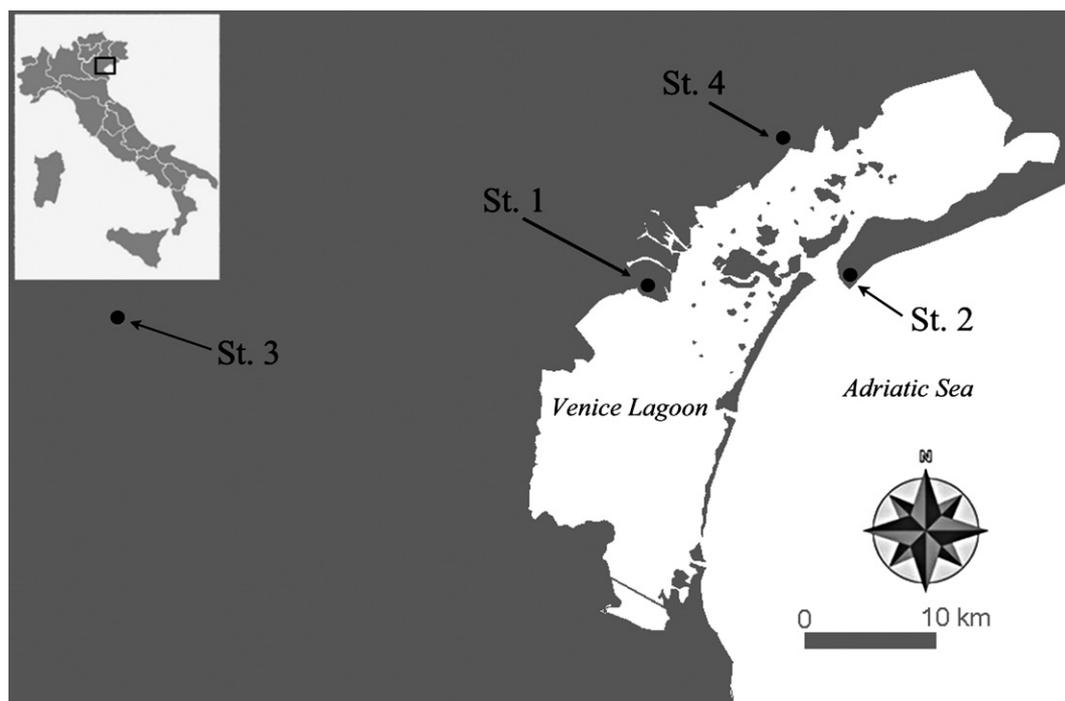


Fig. 1 Sampling sites in the Venice Lagoon area.

using a polyethylene cutter. The aerosol samples were then closed in washed petri dishes inside plastic bags and stored at $-20\text{ }^{\circ}\text{C}$ until analysis. Acid cleaned low density polyethylene (LPDE) bottles were used to store the digested samples. Blank filters were washed, dried and weighed following the same analytical protocol used for the sample filters.

Sample treatment and procedure

The sample digestions were carried out in a microwave oven (Milestone model Ethos 1600) provided with a ten places rotor (HPR 1000/10S) and 100 ml TMF (tetrafluoromethoxy) vessels. Reagents used for sample digestion were ultra pure grade (Ultrapure HCl, HNO_3 and HF supplied from Romil Ltd Cambridge).

Before sample digestion the TMF vessels were filled with 10 ml supra pure 67–69% HNO_3 and cleaned with a three step digestion programme (step 1: 5 min at 300 W; step 2: 5 min at 0 W; step 3: 5 min at 400 W). After digestion the solutions were diluted to a final volume of 25 ml with ultrapure water in acid cleaned LPDE bottles for the determination of trace elements by ICP-QMS. A reagent blank, composed of the same amounts of chemicals used in the sample digestion, was included in each sample digestion batch to monitor the cleanliness of microwave digestion and sample handling processes during digestion.

Instrumentation and quantification

Al, As, Ca, Cd, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Sr, V, and Zn were determined by inductively coupled quadrupole mass spectroscopy (Agilent model 7500) equipped with a double pass spray chamber in PFA fitted with the Agilent V-groove nebulizer and a torch with a ceramic injector tube, resistant to hydrofluoric acid.

Prior to use the ICP-QMS spectrometer was tuned to obtain CeO^+/Ce^+ ratio $<0.5\%$ and $\text{Ce}^{2+}/\text{Ce}^+$ ratio $<2\%$ ¹⁰ with the sample introduction system in place. The carrier gas flow rate was optimised to maximize the sensitivity for ^7Li , ^{89}Y , and ^{205}Tl and minimize the CeO^+ and Ce^{2+} signal. The best signal to noise ratio

Table 1 Instrumental conditions and measurement parameters for the Agilent 7500 inductively coupled plasma quadrupole mass spectrometer

RF power	1450 W
Spray chamber temperature (S/C)	$2\text{ }^{\circ}\text{C}$
Carrier gas flow rates	1.1 L min^{-1}
Ion sampling depth	Optimised to obtain minimum interference signal intensity (8 mm)
Selected isotopes	^7Li , ^{23}Na , ^{24}Mg , ^{27}Al , ^{39}K , ^{44}Ca , ^{51}V , ^{53}Cr , ^{55}Mn , ^{57}Fe , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{67}Zn , ^{75}As , ^{85}Rb , ^{88}Sr , ^{111}Cd , ^{133}Cs , ^{208}Pb
Sample uptake rate	0.5 ml/min
Washing time	3 min
Take up time	45 s
Integration time per point	1 s for Cs, Li, Rb; 0.5 s for Cd, Co; 0.2 s for As, Cr, Cu, Mn, Ni, Sr, V; 0.1 s for Al, Ca, Fe, K, Mg, Na, Pb, Zn
Number acquisition points per peak	3

was found to be between a flow rate of 1.0 and 1.2 L min^{-1} . Since the determined elements are present in aerosol samples at very different concentrations, differentiated integration times (see Table 1) were used to optimise the instrumental sensitivities for each element.

Quantification was performed using matrix-matched calibration curves prepared by using multi-element standard solutions for As, Cd, Co, Cr, Cs, Cu, Li, Mn, Ni, Pb, Rb, Sr, V, Zn, and by single element standard solutions for Al, Ca, Fe, K, Mg and Na. Every analysis cycle calibration curve was prepared using one blank sample where 11 additions were carried out to cover the entire concentration range of elements in the aerosol samples. The following range of concentrations were used: $0.005\text{--}200\text{ }\mu\text{g L}^{-1}$ for As, Cd, Co, Cr, Cs, Cu, Li, Mn, Ni, Pb, Rb, Sr, V, Zn, and $100\text{--}1000\text{ }\mu\text{g L}^{-1}$ for Al, Ca, Fe, K, Mg and Na. A $100\text{ }\mu\text{g L}^{-1}$ Os and Ru solution was added on line using a T-piece and was used as an internal standard during calibration and sample analysis. Multi-element standard solution of metals (10 mg L^{-1}) were supplied from Ultra Scientific (North Kingstown, RI, USA). Single-element standard solutions were supplied from SPEX CertiPrep. INC. Metuchen (Os and Ru, 10 mg L^{-1}) and from Ultra Scientific (Al, Ca, Fe, K, Mg, Na 1000 mg L^{-1}). For each sampling campaign the blank concentration was measured and used to correct the concentration measured in the dissolved filters.

Results and discussion

Blanks and detection limits

Several blanks were collected under particular conditions to better evaluate the contributions from handling, exposure and treatment of the filter and to establish baseline concentrations, which were then subtracted from the concentrations of trace elements in the exposed filters.

The contribution to the blank values from filter handling during aerosol sampling was evaluated by keeping the filters in the samplers at the sampling station for a few minutes without any air flowing and then transferring them to a plastic bag without any further exposure. These blanks, defined field blanks (FBs), were then treated and analysed following the procedure applied to the samples.

Since sampling of the aerosol was carried out only when the wind blew in particular conditions the samplers remained inactive for long time periods. To estimate the contribution to the blank values by passive deposition, the filters were kept at the sampling stations for fifteen days without any air flow. These blanks, defined campaign blanks (CBs), were then treated and analysed as the aerosol samples. In order to emphasize the effect of handling during aerosol sampling, measurements of blank concentration of some elements in filters washed and maintained always inside the class 100 clean area were carried out (filter blank).

The amounts of trace metals found in cellulose slotted filters used as filter blanks, field blanks and campaign blanks are presented in Table 2. The values found in FBs and CBs ranged from $0.0006\text{ }\mu\text{g/filter}$ of Cs to $27\text{ }\mu\text{g/filter}$ of K for the campaign blanks and from $0.0006\text{ }\mu\text{g/filter}$ of Cs to $11\text{ }\mu\text{g/filter}$ of Na for the field blanks. One anomalous result was obtained

Table 2 Mean amounts of elements ($\mu\text{g}/\text{filter}$) and standard deviation (SD) measured in campaign blanks (CBs) and field blanks (FBs) of slotted filters for the whole processes of sampling, treatment and analysis

Element	Campaign blanks		Field blanks		Filter blank	
	Mean ^a	SD ^b	Mean ^a	SD ^b	Mean ^a	SD ^b
Al	3	1	2.0	0.7	0.07	0.04
As	0.09	0.01	0.47	0.07		
Ca	8	2	2.6	0.7		
Cd	0.006	0.0007	0.002	0.001		
Co	0.0045	0.0005	0.005	0.002		
Cr	0.23	0.04	0.6	0.2		
Cs	0.0006	0.0001	0.0006	0.0005		
Cu	0.07	0.01	0.05	0.03	0.04	0.03
Fe	5.1	0.3	3.1	0.8		
K	27	3	2.9	0.7		
Li	0.004	0.001	0.013	0.003		
Mg	0.8	0.2	0.5	0.1		
Mn	0.04	0.01	0.05	0.02	0.007	0.005
Na	15	2	11	3		
Ni	0.05	0.01	0.11	0.05		
Pb	0.021	0.003	0.022	0.006	0.005	0.004
Rb	0.0047	0.0007	0.004	0.002		
Sr	0.024	0.009	0.011	0.008		
V	0.016	0.008	0.07	0.02	0.01	0.008
Zn	1.6	0.5	0.4	0.1	0.24	0.12

^a Mean. ^b Standard deviation values calculated by 7 repeats for campaign blank, 12 repeats for field blank and 5 repeats for the filter blank.

for arsenic, the concentration in the field blank was about five time higher than the campaign blank. The concentrations of elements measured in filter blank were for larger part of element determined significantly lower than FBs and CBs; therefore is evident that handling the membrane for exposition, transport and settling they on the samplers may contribute significantly at the blank concentration. In spite of the long contact of the CBs with the sampler no positive trend was observed with respect to FBs, therefore the contribution to the trace elements blank from passive deposition and contact with the sampling system is considered as negligible. Since FBs are easier to collect, they were used to quantify the “limit of detection” (LOD), which was calculated as 3 times the standard deviation values of the blank content, an average air volume of 4449 m³ was used to calculate the LOD in term of ng m⁻³.¹¹ The FBs average blank values for back filters are presented in Table 3. The amounts found ranged from 0.002 $\mu\text{g}/\text{filter}$ for Cs to 24 $\mu\text{g}/\text{filter}$ for Na.

Slotted filters, which have a lower content of cellulose than back filters, show lower blank values (Table 2 and Table 3) for the almost all elements so different blank corrections must be used for the first five fractions (slotted filters) and for the final fraction (size <0.49 mm) (back filters).

Comparison with limits of detection previously published shows that our results are comparable with values reported in the literature. The LODs reported by Yang *et al.*⁷ ranged from 0.015 ng m⁻³ for Cd to 46 ng m⁻³ for Ca using microwave digestion and ICP-MS analysis. Fernández Álvarez⁸ reported LOD values ranging between 0.025 ng m⁻³ for As to 0.94 ng m⁻³ for Pb using microwave digestion and inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES). Detection limits found by A. A. Karanasiou *et al.*⁶ range from 0.0004 ng m⁻³ for Cd to 4.3 ng m⁻³ for Al using microwave digestion and electrothermal atomic absorption spectroscopy analysis (ETAAS).

Table 3 Mean amounts of elements ($\mu\text{g}/\text{filter}$), standard deviation (SD), limit of detection (LOD ng m⁻³) estimated by back filter field blanks

Element	Field blanks		
	Mean ^a	SD ^b	LOD ^c
Al	3	1	0.7
As	0.65	0.06	0.04
Ca	4.5	0.8	0.5
Cd	0.004	0.002	0.002
Co	0.005	0.001	0.001
Cr	0.7	0.1	0.1
Cs	0.002	0.001	0.001
Cu	0.09	0.03	0.02
Fe	3.9	0.5	0.3
K	4.1	0.5	0.3
Li	0.017	0.003	0.002
Mg	0.9	0.3	0.2
Mn	0.05	0.01	0.008
Na	24	1	1
Ni	0.09	0.03	0.02
Pb	0.04	0.02	0.01
Rb	0.007	0.002	0.001
Sr	0.015	0.008	0.006
V	0.09	0.02	0.02
Zn	1.0	0.4	0.3

^a Mean. ^b Standard deviation values calculated by 7 independent part of filters at least. ^c LOD in ng m⁻³ was calculated as three times the blank standard deviation and using an average air volume of 4449 m³.

Accuracy and repeatability

Several microwave digestion programs with different combinations of power and time settings and different reagent mixtures were tried to achieve complete dissolution of the particulate matter. The best recoveries were obtained by the following step program settings of microwave oven: step 1: 10 min at 250 W; step 2: 1 min at 0 W; step 3: 20 min at 400 W; step 4: 2 min at

0W; step 5: 20 min at 500 W, step 6: 2 min at 0 W; step 7: 3 min at 650 W and two acid mixtures (a) and (b):

(a) 1.5 ml ultra pure water, 5 ml HNO₃ and 1 ml HF (Romil Ultrapure acids);

(b) 1.5 ml ultra pure water, 5 ml HNO₃, 1 ml HF and 0.5 ml HCl (Romil Ultrapure acids).

In order to validate the microwave digestion methods, portions of 1/6 of a blank back filter were loaded with about 10 mg of Standard Urban Dust Reference Material (NIST, SRM-1648). The reagents were added and the filter and reference material were digested following the selected program settings, the solution was diluted until a final volume of 25 ml by ultrapure water. The procedure was repeated at least five times using different portions of the filter for each of the reagent mixtures listed above as (a) and (b). As, Cd, Cr, Cu, Mn, Ni, V concentrations were quantified using matrix-matched calibration curves without any dilution of the digested NIST sample. Al, Fe, K, Na, Pb and Zn concentrations were quantified after a 1:100 dilution of the digested reference material sample using external calibration curves. Experimental values and certified values are compared in Table 4. For most of the elements satisfactory agreement between the measured and certified values was found using both the reagent mixtures. Recoveries of the elements content, expressed as a percentage of the NIST certified values, ranged from 79% for Cr to 120% for Zn in samples digested with the H₂O, HNO₃ and HF mixture and from 84% for V to 105% for K in sample digested with the H₂O, HNO₃, HF and HCl mixture. Since no significant difference was found for the two reagent mixtures tested, sample digestion without HCl were preferred to minimize the interference from ⁴⁰Ar³⁵Cl⁺ in the determination of As.

Dividing the filters into small sections was necessary to avoid the overloading microwave vessels due to the large weight of the cellulose filters (from 1.4 g for slotted filters to 4 g for back-filters). The back filters were divided into six equal sections and slotted filters were divided into four equal sections. Since only one section was used to assess the sample concentration, the uniformity of atmospheric particulate distribution on the filters was tested by digestion and analysis of different sections of the same aerosol sample. The results obtained for digestion and analysis of four

Table 5 Results (ng m⁻³), mean values and standard deviation (SD) of elemental content in tests of uniformity of aerosol samples. Digestion and analysis were performed on four sections of a sample collected on a back filter^a

Element	Results ng m ⁻³ in repeatability tests	Mean	SD
Al	31.4, 31.1, 31.4, 32.3	31.5	0.5
As	u.d.l.	u.d.l.	u.d.l.
Ca	14.6, 14.9, 16.3, 16.3	15.5	0.9
Cd	0.18, 0.22, 0.23, 0.20	0.21	0.02
Co	0.0095, 0.0093, 0.0103, 0.0095	0.0096	0.0004
Cr	0.16, 0.19, 0.19, 0.25	0.20	0.04
Cs	0.0107, 0.0112, 0.0119, 0.0103	0.0110	0.0007
Cu	0.62, 0.68, 0.74, 0.77	0.70	0.07
Fe	26, 28, 31, 30	29	2
K	52, 61, 62, 55	58	5
Li	0.0269, 0.0264, 0.0272, 0.0272	0.0270	0.0004
Mg	8.1, 8.0, 8.6, 8.5	8.3	0.3
Mn	0.93, 1.02, 1.07, 1.00	1.01	0.06
Na	17.6, 18.4, 17.7, 16.7	17.6	0.7
Ni	0.79, 0.97, 0.98, 0.89	0.91	0.09
Pb	3.0, 3.7, 3.8, 3.3	3.5	0.4
Rb	0.14, 0.16, 0.17, 0.15	0.16	0.01
Sr	0.119, 0.127, 0.137, 0.132	0.129	0.008
V	1.6, 1.9, 2.0, 1.7	1.8	0.2
Zn	6.3, 7.3, 7.2, 6.9	6.9	0.4

^a u.d.l.: under detection limit.

sections of a randomly chosen aerosol sample collected on a back filter are reported in Table 5. The relative standard deviations of element concentrations measured for most elements was less than 10% showing that the sampled atmospheric particulate can be considered uniformly distributed on the filters and that a section of the filter is representative of the entire sample.

Determination of trace elements in the atmospheric aerosol of the Venice Lagoon

In order to test the methodology to characterize aerosols with remarkable different composition, the procedure was applied to

Table 4 Elemental contents (µg g⁻¹) and percent of recovery obtained for the certified urban particulate (NIST 1648), dissolved by microwave-assisted digestion with two different acid mixtures^{d,e}

Element	Certified values ^b	Found values ^{c,d}	Recovery, %	Found value ^{c,e}	Recovery %
Al ^a	3.42 ± 0.11	3.2 (0.1)	94	3.12 (0.05)	91
Fe ^a	3.91 ± 0.10	3.6 (0.1)	92	4.0 (0.4)	102
K ^a	1.05 ± 0.01	1.1 (0.2)	105	0.84 (0.04)	80
Na ^a	0.425 ± 0.002	0.40 (0.01)	94	0.41 (0.01)	96
Pb ^a	0.655 ± 0.008	0.59 (0.01)	90	0.63 (0.01)	96
Zn ^a	0.476 ± 0.014	0.48 (0.02)	101	0.57 (0.02)	120
As	115 ± 10	101 (3)	88	105 (3)	91
Cd	75 ± 7	66 (1)	88	67 (2)	89
Cr	403 ± 12	370 (16)	92	320 (29)	79
Cu	609 ± 27	550 (11)	90	560 (15)	92
Mn	786 ± 17	780 (10)	99	760 (36)	97
Ni	82 ± 3	78 (2)	95	68 (3)	83
V	127 ± 7	107 (3)	84	110 (4)	87

^a Content in weight percentage (w/w %). ^b Average ± 95% tolerance limits. ^c Average (standard deviation). ^d Digestion acid mixture: 1.5 ml H₂O, 5 ml HNO₃, 0.5 ml HCl, 1 ml HF (Romil Ultrapure acids). ^e Digestion acid mixture: 1.5 ml H₂O, 5 ml HNO₃, 1 ml HF (Romil Ultrapure acids).

determine major and trace element concentrations in the PM10 and to define the distribution between fine (aerodynamic diameter <3 µm) and coarse particles (aerodynamic diameter >3 µm) in the atmosphere aerosols collected in areas of the Venice region characterized by airborne particulate of different origin.

Mean values of PM10 and of element concentrations during the entire sampling period are summarized in Table 6. Similar PM10 mean mass concentrations at sites 1, 2 and 4 were obtained during the four sampling campaigns (39.3 µg m⁻³, 21.0 µg m⁻³ and 34.2 µg m⁻³ respectively), while, a higher median value (56.5 µg m⁻³) was obtained at station 3 (rural area), that was ascribed to occasional fires occurring during the summer season in the neighbouring wood. The results are consistent with those reported for other urban-industrial sites in Europe. Rössli *et al.*¹² found in Basel (Central Europe) a mean mass concentration of 28.3 µg m⁻³, Viana *et al.*¹³ measured at Ghent in west Europe a mass concentration of 28.6 µg m⁻³ during winter 2005 and at Barcelona in the Mediterranean a mass concentration of 34.0 µg m⁻³ during winter 2004. Higher values (78–89 µg m⁻³) are found by Voutsas *et al.*¹⁴ at Thelassoniki in Greece during the summer 1997–1998 and by Weckwerth¹⁵ (54 µg m⁻³) in the atmosphere of Cologne (Germany).

Measured elemental concentrations differ by several orders of magnitude from one metal to another. In relation to their crustal abundance, the highest concentrations are observed for Al and Fe at the µg m⁻³ level, whereas the lowest concentrations, in agreement with their very low crustal abundance, are observed for elements such as Cs, at the sub-ng m⁻³ level.¹⁶

The ratio between highest and the lowest concentration detected for trace elements cover an interval ranging between 3 to 15. Comparison with relevant data from other urban sites

shows that the trace element concentrations observed in this study are consistent and close to the ones detected in the aerosol of other cities of the central and northern Europe. Concentrations of As, Cd, Ni, Pb and Zn in the PM10 are comparable with those measured in Basel during 97–98, (1 ng m⁻³ for As, 1 ng m⁻³ for Cd, 9 ng m⁻³ for Ni, 55 ng m⁻³ for Pb, 84 ng m⁻³ for Zn),¹² in Edinburgh during 1999–2000 (0.4 ng m⁻³ for As, 0.34 ng m⁻³ for Cd, 3.4 ng m⁻³ for Ni, 14.1 ng m⁻³ for Pb, 1.1 ng m⁻³ for V, 13.3 ng m⁻³ for Zn)¹⁷ and in Budapest during spring 2002 (0.99 ng m⁻³ for As, 27 ng m⁻³ for Pb, 2.8 V ng m⁻³, 90 ng m⁻³ for Zn).¹⁸

The particle content and trace element concentration in the fine and coarse fractions are reported in Table 6. The element distribution between fine and coarse is consistent with sources; fine particle concentrations account for 87% (site 2), 87% (site 3), 77% (site 1) and 83% (site 4) of the PM10 particle mass. All the elements that are prevalently originating from anthropogenic sources such as automotive traffic, oil combustion or industrial processes (As, Cd, Cr, Ni, Pb, V, Zn) are essentially associated to the fine particle fraction (70–95%). On the other hand, elements such as Al and Fe that are mainly from natural sources (soil dust) were almost equally distributed in fine and coarse fractions.

The highest PM10 metal concentration for almost all of the elements was found at station 1 downwind of the large industrial zone of Porto Marghera where the main activities are petrochemical production and refining, iron and steel industries with incineration and thermal plants (fed by fossil fuels). Moreover the site is affected by the vehicular and urban emissions of Mestre.

The concentrations of all the elements, except Na, in the samples collected at site 2, are lower than those measured at St.1 by a factor of 2–4.

Table 6 Mean particle content (µg m⁻³) and trace element concentration (ng m⁻³) in PM10, coarse and fine fractions of particulate airborne collected in marine, rural, urban and industrial areas of Venice during four campaigns from March 2002 to June 2003

	Site 1 (industrial-urban area)			Site 2 (marine area)			Site 3 (rural area)			Site 4 (urban area)		
	PM10	Coarse	Fine	PM10	Coarse	Fine	PM10	Coarse	Fine	PM10	Coarse	Fine
Particulate	39.3	8.98	30.3	21.0	2.67	18.3	56.5	7.28	49.2	34.2	5.91	28.3
Al ^a	0.468	0.180	0.289	0.117	0.046	0.071	0.221	0.111	0.109	0.085	0.039	0.046
As	4.2	0.25	4.0	0.40	0.046	0.35	0.81	0.046	0.76	5.9	0.23	5.7
Ca ^a	0.88	0.44	0.44	0.135	0.097	0.038	0.21	0.121	0.086	0.27	0.155	0.118
Cd	2.5	0.2	2.3	0.42	0.012	0.41	0.81	0.22	0.59	2.9	0.18	2.7
Co	0.38	0.101	0.28	0.056	0.0176	0.039	0.167	0.035	0.133	0.091	0.028	0.064
Cr	2.3	0.47	1.9	0.45	0.13	0.32	1.2	0.13	1.1	1.2	0.19	1.0
Cs	0.029	0.0077	0.021	0.0078	0.0012	0.0066	0.0099	0.0018	0.0081	0.017	0.0031	0.014
Cu	14	5.0	9.0	3.4	0.94	2.5	9.1	3.7	5.5	8.7	2.6	6.1
Fe ^a	0.48	0.20	0.28	0.130	0.046	0.084	0.21	0.083	0.124	0.21	0.074	0.136
K ^a	0.31	0.071	0.24	0.13	0.025	0.106	0.18	0.034	0.15	0.25	0.029	0.22
Li	0.508	0.153	0.355	0.078	0.029	0.048	0.118	0.043	0.075	0.102	0.033	0.069
Mg	259	124	135	80	51	29	111	63	49	91	49	42
Mn	24	9.9	13.7	4.8	1.2	3.6	9.2	2.76	6.4	7.1	1.9	5.2
Na ^a	0.36	0.151	0.206	0.36	0.25	0.108	0.21	0.090	0.120	0.198	0.097	0.101
Ni	17	2.9	14	3.3	0.49	2.8	3.1	0.38	2.7	2.2	0.36	1.9
Pb	29	4.9	24	11	0.85	10	17	1.9	15	20	1.7	18
Rb	0.98	0.27	0.72	0.42	0.076	0.35	0.63	0.15	0.49	0.71	0.098	0.61
Sr	2.6	1.2	1.41	0.84	0.46	0.39	1.37	0.56	0.81	0.89	0.43	0.46
V	14	2.2	12	7.3	0.88	6.4	4.5	0.26	4.3	2.2	0.25	1.9
Zn	108	30	79	31	3.4	28	58	10.8	47	54	7.5	47

^a Mean concentration in µg m⁻³.

Conclusions

The proposed method of aerosol sampling, sample microwave digestion and inductively coupled mass spectroscopic analysis allows accurate determination of a large number of elements at trace levels in minute amounts of aerosol samples. The microwave digestion procedure with a simple acid mixture, containing only HNO₃ and HF, was validated using the certified reference material NIST SRM 1648 (Urban Particulate Matter). The results show that it is an efficient method for the determination of trace elements in airborne particles with element recoveries always higher than 80% for all the analysed elements. The contributions of different processes to the blank were evaluated to identify possible sources of sample contamination. The results show that the blank contributions from filter handling and sampling procedures are critical and must be controlled for a correct evaluation of the analytical results. The contribution is significant from the filter handling, transport and settling on the sampling system, while the contributions to the blank values by passive deposition is negligible therefore blank contributions can be evaluated by placing filters on the sampling device at every sampling station for some minutes without any air flow. The measured LODs for the method allow the determination of trace elements in aerosol in the range of concentrations observed in the four areas characterized from aerosol of different origin if the sampled air-volume is 1000 m³ or higher.

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