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Comparison of extracting solutions for elemental fractionation in airborne particulate matter

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ABSTRACT

It is here described the comparison of extraction efficiency of some solutions (acetate buffer, deionized water, diluted HNO_3 and EDTA) frequently adopted in literature for evaluating the elemental solubility in airborne particulate matter. This comparison was performed considering the distribution of As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Na, Ni, Pb, S, Si, Sb, Sn, Sr, Ti, V, Zn between the extractable and mineralized residual fractions on the NIST 1648 certified material, PM_{10} real samples and size-segregated samples, collected by a 13-stage impactor.

The extracting solutions were evaluated by comparing extractive efficiencies and robustness towards some factors, such as acidity and concentration of complexing species, that have great environmental variability and that could be able to modify the extractive efficiency.

Furthermore, extraction methods application to size-segregated samples allowed estimating the selectivity of extracting solutions towards dimensionally characterized emission sources, as dusts originated from abrasion and road dust re-suspension.

On the basis of the obtained results, it was possible to define the main advantages and disadvantages resulting from the use of different extracting solutions, necessary to make possible the comparison of environmental studies carried out in different extractive conditions and to start up a proper study for harmonizing extracting procedures.

1. Introduction

During the last years, the application of speciation methods and elemental chemical fractionation to environmental monitoring, concerning airborne particulate matter (PM), has been increasing its diffusion [1–5]. In fact, it is widely recognized that the capacity to fractionate the total elemental content, according to different chemical and physical characteristics of single elements, is a valid instrument for improving studies both on emission sources identification [6–8], and on health and environmental impact [9–11]. However, due to the great spatial and temporal variability of PM chemical composition, the possibility to take general conclusions is strictly connected to a capillary and time protracted analytical control. Moreover, the scanty sample quantities that are generally available and high sampling costs force to utilize micro analytical, and possibly multiparameter, procedures.

Even if it is evident that the sole stringent methodical use of chemical speciation [1,12–16] could allow a complete understanding of toxicological and environmental impact of every single emission source, the adoption of streamlined chemical fractionation procedures is frequently applied in order to guarantee an easier, faster and cheaper utilization to extended monitoring campaign.

Different studies about the application to PM samples of Tessier extracting scheme or of its successive adaptions, taylored for soil and sediments, have been published [1,3,14,16–20]. Even if it is recognized that the chemical significance of the fractions obtained is strongly reduced in PM, these studies have demonstrated that the most interesting and representative fractions are the most soluble and the residual ones [3–5,17,21,22]. So, elemental distribution evaluation between two fractions, being one extractable in water solutions and the other residual, is considered a good compromise among costs, analytical times and achievable information. However, different extracting solutions were suggested and adopted for the evaluation of the extractable fraction of PM, thus reducing the possibility to compare results given in distinct geographical areas and environmental conditions [23–28].

The extracting solution choice was often influenced by the attempt to mime conditions of PM interactions either with environmental [2,29] or biological systems [4,17,21,30], and the extraction in water [4,17,22,28,31–40] and/or in diluted strong acids is rather diffused [6,21,22,28,31–33,41,42]. Anyway, the wide variability and complexity of the natural processes acting on the solubility equilibria of metals in atmospheric particles prevents the iden-

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Table 1
Comparison of extracting solutions used, pH of solutions before and after leaching of PM_{10} samples and sulphate concentrations in PM_{10} extracted fraction.

PM_{10} Sampling period	Extracting solutions	pH		SO_4^{2-} (μg/m^3)
		Before extraction	After extraction (minimum–maximum)	Extractable fraction (minimum–maximum)
All periods	Acetate buffer 10 mM (solution A)	4.30	4.29–4.34	1.35–6.08
14–19 October 2006	Deionized water (solution B)	6.44	3.80–4.47	1.61–4.51
11–24 January 2007	Nitric acid 0.200 M (solution C)	0.78	0.75–0.79	2.03–6.08
17 February to 2 March 2007	EDTA 1 mM (solution D)	4.77	4.01–4.11	1.35–3.74

tification of an extracting solution able to reproduce realistically the natural bio- and environmental availability of elements. Major interpretative potentialities given applying fractionation methods are then related to their application to source apportionment studies [1,3,6,14,39]. The selectivity increase of elements as source tracers [6,43–45] has then an important value in selecting the extracting solution. Furthermore, when chemical fractionation data are used to improve emission sources traceability, it is important that results are directly related to the emission sources. Some considerations about fractionation robustness towards possible influences by external factors have then to be taken. Among external factors that could influence chemical fractionation, (i) adsorption phenomena on particle surface, (ii) possible complexes formation with other organic and inorganic soluble species present in matrix and (iii) solubility equilibria changes of salts and hydroxides towards acids and basis also present in the matrix, have to be considered.

While water extraction is not expected to be robust towards external factors, the adoption of a strong acid, should allow a good control of all these effects. In our laboratory, it has been utilized an extracting solution at buffered pH and weekly complexing (acetate buffer) [46–50], that is not influenced by acids and basis present in the matrix. This solution allowed us to obtain good results for traceability of some emission sources classes [43,44].

This work is about the comparison between extracting behaviour of acetate buffer solution with that of H_2O and nitric acid, the most diffused solutions in literature, in order to make easier results comparison, obtained by different research groups, and set in place the basis for future harmonizing procedures. The study was also extended to the adoption of a polydentate chelant (ethylenediaminetetraacetic acid—EDTA), supposed to be more efficacious than acetate buffer in competing with adsorption and complexing equilibria [26,51].

Besides, the extracting efficiencies evaluation on certified material (NIST 1648) and PM_{10} real samples (so to highlight possible dependences from environmental variability in the matrix), selectivity estimation of chemical fractions towards emission sources was attempted by examining relations between elemental solubility, emission sources and particles dimensions. At this aim, extractive efficiencies in PM size-segregated samples (collected by a 13-stage inertial impactor) were also considered.

2. Experimental

2.1. Materials and reagents

The following reagents were used: ultrapure deionized water (MilliQ), nitric acid (65%, suprapur, Merck KGaA, Darmstadt, Germany), hydrogen peroxide (30%, Suprapur, Merck KGaA, Darmstadt, Germany), glacial acetic acid (>99.9%, Carlo Erba Reagenti Spa, Rodano (MI), Italy), potassium acetate (SigmaUltra, ≥99.0%, Sigma–Aldrich Inc., St. Louis, MO, United States), ethylenediaminetetracetic acid disodium salt (RPE, Carlo Erba Reagenti Spa, Rodano (MI), Italy), disodium carbonate, Na_2CO_3 (Merck KGaA, Darmstadt, Germany), sodium hydrogen carbonate, $NaHCO_3$ (Merck KGaA, Darmstadt, Germany).

2.2. Sampling procedure

2.2.1. PM_{10} sampling

24-h samplings of PM_{10} particulate matter were carried out during the periods, October 2–19, 2006, January 11–24, 2007 and February 17 to March 2, 2007, at an urban site located inside the area of University of Rome "La Sapienza", about 50 m from the nearest urban road but affected by local traffic (parking sites), by means of a HYDRA Dual Sampler (FAI Instruments, Fontenuova, Rome, Italy). Two sampling heads, complying with specifications of the ENI 12341 regulation (flow rate 2.3 m^3/h), were used. HYDRA Dual Sampler is an automatic and sequential sampling system on two independent sampling channels, both equipped with 47 mm diameter PTFE membranes, 1 μm pore size (Pall Corporation, MI, USA).

The equivalent sample pairs so obtained were stored in sealed (Gelman Sciences Inc., MI, USA) vessels at 4 °C until analysis.

2.2.2. Multi-stage impactor sampling

For size-segregated sampling, a 13-stage low-pressure cascade impactor (DLPI, DEKATI Ltd., Tampere, Finland) was run during 14 d periods, at the same sampling site. During the periods January 11–24, 2007 and February 17 to March 2, 2007, two samplings were carried out, at the same time as the PM_{10} ones. The instrument operated at the flow rate of 10 L min^{-1} and at the pressure of 100 mbar, under the last impactor stage. Nominal values for the equivalent aerodynamic 50% cut-off diameters (AD) of the impactor stages are: 10, 6.8, 4.4, 2.5, 1.6, 1.0, 0.65, 0.40, 0.26, 0.17, 0.108, 0.060 and 0.030 μm. PTFE membranes, 25 mm diameter (ALBET, Barcelona, Spain) were used as substrates on collection plates of the impactor. Collection substrates of impactors are generally greased to reduce bounce and blow-off of particles; however, for this study, it was not decided to add any grease in order to improve analytical quality of the measurements [43].

2.3. Analytical procedure and data consistency

Extracting solutions considered for this work are presented in Table 1, which also shows ranges of variability both for pH and sulphate (SO_4^{2-}) concentrations, estimated after PM_{10} samples extraction.

HNO_3 at 0.200 M concentration [32,42] was chosen in order to enhance the extracting behaviour of this strong acid solution. Acetate buffer solution (CH_3COOK/CH_3COOH) was 0.010 M at pH 4.30. This pH is very similar to the PM spontaneous one, so to ensure an effective control of extracted solution pH. On the basis of some preliminary tests, for minimizing alkaline-earth ions complexation (Ca^{2+} and Mg^{2+}), which are present at high concentrations in PM, a weakly acidic pH for EDTA (disodium salt) solution was used. In this way, a low EDTA concentration (1 mM) is enough to ensure the presence of an excess of free chelating agent in solution, avoiding interferences in ICP analysis.

Table 2
Number of valid pairs (*N*), mean values (mean), variability range (minimum–maximum), relative repeatability (r_{rel}) and linear regressions values *A* vs. *B* (Pearson coefficient R^2, slope and intercept) concerning total elemental concentrations (extractable and mineralized residual) of 46 PM_{10} pair samples.

	N	Arithmetic mean (ng/m^3)	Minimum–maximum (ng/m^3)	r_{rel} (%)	R^2	Slope	Intercept (ng/m^3)
As	31	0.78	nd[a]-4.2	22	0.780	0.93	0.06
Ba	46	8.3	1.0–19.2	6.2	0.987	0.94	0.54
Cd	46	0.33	0.1–3.2	9.6	0.997	1.07	−0.018
Co	36	0.19	nd[a]-0.36	7.2	0.930	0.92	0.013
Cr	46	4.7	1.5–10.3	6.5	0.957	0.90	0.53
Cu	46	18	1.8–66.2	4.3	0.996	0.97	0.42
Fe	46	332	29–858	8.7	0.988	0.91	35
Mg	46	126	12–433	4.6	0.993	0.98	3.4
Mn	45	7.7	2.9–22.4	4.9	0.985	0.99	0.18
Ni	32	4.2	nd[a]-8.2	18	0.761	0.93	0.4
Pb	46	9.5	2.8–35.2	8.3	0.969	1.05	−0.97
S	46	1059	477–2028	6.9	0.965	0.90	46
Sb	46	5.2	0.50–20.2	5.3	0.993	1.01	−0.075
Sn	46	2.5	0.51–6.9	8.5	0.962	0.93	0.19
Sr	46	3.6	0.34–8.3	5.7	0.987	0.95	0.22
Ti	46	6.6	0.67–26.1	9.3	0.937	0.92	1.1
V	46	2.7	0.72–6.7	4.0	0.990	1.01	−0.059
Zn	46	53	17–113	16	0.801	0.93	3.9

[a] Not detected.

Trials on Urban Particulate Matter NIST 1648 reference material (National Standard Institute of Technology, USA) were performed weighting different amounts ranging from 2 to 5 mg of powder by means of an analytical scale (Sartorius M5P-F, Sartorius, Goettingen, Germany; sensibility 1 μg). Before analysis, PM_{10} filters were removed from the poly-methylpentene support ring by means of a ceramic blade.

NIST and PM_{10} samples were then extracted in ultrasonic (US) bath (28/34 kHz, 80/180 W) for 15 min, using different selected extracting solutions. US-assisted extraction is needed to favour an efficient contact of the solution with particles included in the hydrophobic filter membrane. The solution (extractable fraction) was broken apart the solid residue by a 0.22 μm filtration (NC 25 mm diameter Millipore, MA, USA), and analyzed by inductively coupled plasma-optical emission spectrophotometer (ICP-OES Axial Varian VISTA MPX, Varian Analytical Instruments, Mulgrave, Victoria, Australia) equipped with an ultrasonic nebulizer (U 5000 AT+, Cetac Technologies Inc., Omaha, NE, USA). An external matrix-matched calibration adopting Y as internal standard was always used for ICP-OES measurements. Operative blank values obtained with HNO_3, EDTA and deionized water were equivalent or lower than those previously reported for acetate buffer [50]. pH measurements of solutions in equilibrium with samples were made on parts of extracts, after filtration, using a pH-meter (Basic 20, Crison Instruments, Alella, Barcellona, Spain) daily calibrated and equipped with a Crison 52-02 pH electrode.

The solid residue was quantitatively recovered and then digested in microwave (MW) oven (Milestone Ethos Touch Control, Rockford, Illinois, USA, with HPR 1000/6S rotor) with a HNO_3:H_2O_2, 4:2 mixture; the obtained solution (mineralized residual) and the insoluble residue were separated on a 0.45 μm filter (NC 25 mm diameter Millipore) and analyzed by ICP-OES. The same digestion procedure was also applied in direct digestion of NIST 1648. This procedure was previously fully described and validated [46–50] and allows a good recovery from the reference material for all the reported elements, with the only exception of Cr. The use of HF in the digestion mixture, necessary to obtain a total dissolution of sample [52,53], was avoided to achieve a better analytical repeatability and lower limits of detection and quantification. For the same reasons, HNO_3/H_2O_2 mixture is also suggested by CEN for the determination of Pb, As, Ni and Cd in PM samples [54].

One twin of equivalent PM_{10} samples pairs was always extracted with solution A while the other one, as specified in result and discussion, alternatively with solutions B, C or D. Obtained data consistency was checked by assessment of total elemental concentrations (as sum of extractable and mineralized residual) on each couple members. Results of such elemental analysis check relative to the forty-six PM_{10} samples pairs, object of this work, are summarized in Table 2. Relative repeatability of two couples members, A and B, r_{rel}, was calculated, as suggested in UNI EN14902 [54], as follows:

$$\overline{X} = \frac{\sum_{i=1}^{N}(m_{i\mathrm{A}}+m_{i\mathrm{B}})}{2N}; \quad r = \sqrt{\frac{\sum_{i=1}^{N}(m_{i\mathrm{A}}-m_{i\mathrm{B}})^2}{2N}}; \quad r_{\mathrm{rel}} = \frac{r}{\overline{X}} \times 100$$

where $m_{i\mathrm{A}}$ and $m_{i\mathrm{B}}$ are the masses of the element determined on the *i*th pair of filters A and B and *N* is the number of valid pairs of PM_{10} samples. It can be noticed how total elemental concentrations, determined on two members of equivalent sample pairs, are in a good agreement for all selected elements, with the exception of As, Ni and Zn. Therefore, different concentrations determined in the extractable and mineralized residual may be ascribed, with good reliability, to changes in extracting efficiency of compared solutions. For several samples in the set, concentrations of As, Ni and Co were under limit of detection of the method (LOD evaluated from operative blank values: As = 0.4 ng/m^3; Co = 0.1 ng/m^3; Ni = 1.1 ng/m^3). Ni and Zn show particularly high blank values in the mineralized residual fraction.

With regard to size-segregated samples analysis, it was not possible to obtain equivalent samples, so impactor PTFE membranes were submitted to a different extraction procedure. At the beginning each filter was extracted with solution A, as described above. Residual dust, before being submitted to acidic digestion, was alternately extracted, in a sequential way, with solutions C or D and filtered again. As will be pointed out in the following sections, extracting efficiency of C and D solutions was greater than A; for this reason, the extractable amount by means of C and D solutions was evaluated as sum of these two sequentially extracted fractions. In order to check procedure accuracy, consistency trials of obtained data with those relative to PM_{10} samples pairs, sampled in corresponding periods and directly extracted with the same extractant solutions (A and C or A and D), were made. At this aim, for each element and with every extractant solution, the mean concentration obtained through application of the described procedure to the correspondent 14 PM_{10} daily samples pairs, with that given as sum of evaluated concentrations in 1–12 stages of impactor, were compared, following a previously published procedure [43]. Data reported in Table 3, concerning the comparison between acetate

Table 3
Acetate buffer vs. EDTA comparison. Mean concentrations (ng/m^3) evaluated by means of both sequential extraction of size-segregated samples and by direct extraction of PM$_{10}$ samples pairs.

	Extractable fraction				Mineralized residual fraction			
	Acetate buffer		EDTA		Acetate buffer		EDTA	
	Impactor (ng/m^3)	24 h (ng/m^3)	Impactor (ng/m^3)	24 h (ng/m^3)	Impactor (ng/m^3)	24 h (ng/m^3)	Impactor (ng/m^3)	24 h (ng/m^3)
As	1.3	1.1	1.4	1.3	0.71	0.73	0.63	0.65
Ba	5.9	5.4	6.6	6.4	9.1	9.2	8.4	8.6
Cd	0.16	0.21	0.16	0.22	0.09	0.07	0.08	0.06
Co	0.09	0.08	0.08	0.07	0.34	0.28	0.30	0.27
Cr	0.85	0.84	0.75	0.97	15	15	14	15
Cu	18	17	22	22	25	24	21	21
Fe	23	25	103	109	587	609	556	523
Mg	171	158	176	181	85	89	80	76
Mn	3.5	3.4	4.7	4.5	6.9	7.1	6.3	6.4
Ni	1.6	1.8	1.7	1.8	–[a]	3.1	–[a]	3.3
Pb	4.2	4.2	7.7	7.9	5.6	6.3	2.6	2.4
S	715	798	729	759	99	84	86	80
Sb	2.2	2.5	2.8	2.9	5.3	6.0	4.7	5.6
Sn	0.03	0.03	0.03	0.05	3.6	4.4	3.6	4.1
Sr	3.9	3.5	4.3	3.8	2.3	2.0	1.8	1.6
Ti	0.05	0.07	0.28	0.28	9.1	8.7	8.9	8.5
V	1.0	1.1	1.2	1.3	0.79	0.90	0.65	0.74
Zn	49	38	52	40	35	30	32	24

[a] Not determined (high blank values from impactor).

buffer and EDTA, show no considerable changes between values obtained by PM$_{10}$ samples direct extraction and sum of two sequential extractions on size-segregated samples. Similar results were also achieved for samples used in acetate buffer and nitric acid comparison.

2.4. *Robustness evaluation*

2.4.1. *Cl$^-$ concentration*

Six aliquots of reference material (2–5 mg) were extracted by acetate buffer solutions, after adding to extractant solution growing Cl$^-$ concentrations (from 0 to 50 mg/L NaCl). Similar tests were carried out on five PM$_{10}$ samples pairs, a member of which was extracted with solution A and the other one adopting the same solution added with 10, 20, 30, 40 and 50 mg/L NaCl.

2.4.2. *Dust aging*

Six aliquots of certified material (2–5 mg) were extracted by acetate buffer after 1 (3 aliquots) or 2 (3 aliquots) of 8-h oven-dry cycles (105 °C). For estimating the aging phenomena effect in atmosphere, six PM$_{10}$ samples pairs were used: one twin was kept refrigerated (4 °C, darkness) while the other one was exposed to ambient air for 7 d at changeable temperatures (20–35 °C), relative humidity (20–95%) and gathered solar radiation (0–1000 W m^{-2}).

3. Results and discussion

3.1. *Comparison of extractive efficiencies on reference material*

The utilized certified material (NIST 1648) is made of an urban dust, not dimensionally selected and not supported, certified for total concentrations of Al, As, Cd, Cr, Cu, Fe, Mn, Na, Ni, Pb, Se, V and Zn. Even if this material is not perfectly representative of real samples [48], sample homogeneity and sufficient quantity availability of dust allowed to evaluate the extracting analytical repeatability and to compare extracting efficiencies, obtained with the different solutions considered, on a single sample. Results, achieved on 6 replicated samples, are reported in Fig. 1. Recovery percentages, given adding the extractable and mineralized residual fraction, were calculated in comparison to certified values (Fig. 1—upper panel). As regards non-certified elements (Fig. 1—lower panel), recoveries were estimated in respect to total concentration, determined by direct acidic digestion of sample. Recoveries are close to 100% for all certified elements, with the exception of Cr, whose results, due to the incomplete digestion obtained with the HNO$_3$/H$_2$O$_2$ mixture, have a purely comparative value.

Analytical repeatability is sufficiently good with coefficient of variation as a percent value (CV%) lower than 10% for all the extracting solutions considered and elements, with the exception of As and Ni, whose concentrations are close to limit of detection of the method. Generally, solubility percentages obtained could be interpreted considering the existing acid–base and complexing equilibria. For almost all selected elements, it can be pointed out a major extracting efficiency of C and D solutions, in comparison with A and B ones. The A solution shows a similar or slightly higher extracting efficiency (Cd, Cu, Pb and Zn,) to B one, according to pH differences (pH 4.30 for A solution and pH 5.80 for B one, depending on CRM weighted quantities) and equilibria strength of complexes formation, that these metals are able to form with acetate ion [47,55]. According to its strongly acidic pH and to its oxidizing properties, C solution exhibits a particular high extracting efficiency, with a nearly complete solubilization (major of 60–70%) for many elements (with the exception of Co, Sn, Ti, Cr, Mn, Ni and V), that justify its usage for determining pseudo-total content in some works reported in literature [32,42]. As expected, the EDTA (D solution) extracting efficiency is between those observed in nitric acid and acetate buffer. In particular, it can be noted a solubility increase in comparison with acetate buffer extraction, particularly relevant for Fe, Cu, Pb, Cd, V and Sn, while less evident for Sb.

3.2. *Comparison of extracting efficiencies on real samples*

In case of real samples, unfortunately, it was not possible to directly compare extractive efficiency of the four selected solutions. Therefore, the correlation was performed by comparing the extractive efficiency for different groups of samples, as described in Section 2. The a priori selection of solution "A" as reference one, was made to facilitate interpretation of data obtained, thanks to the confidence also gained from our research group in its use [43,44,46–50]. Fig. 2 shows mean values and range variability of extractable fraction percentages (extracted amount/total amount × 100) given from PM$_{10}$ samples pairs used for extractive

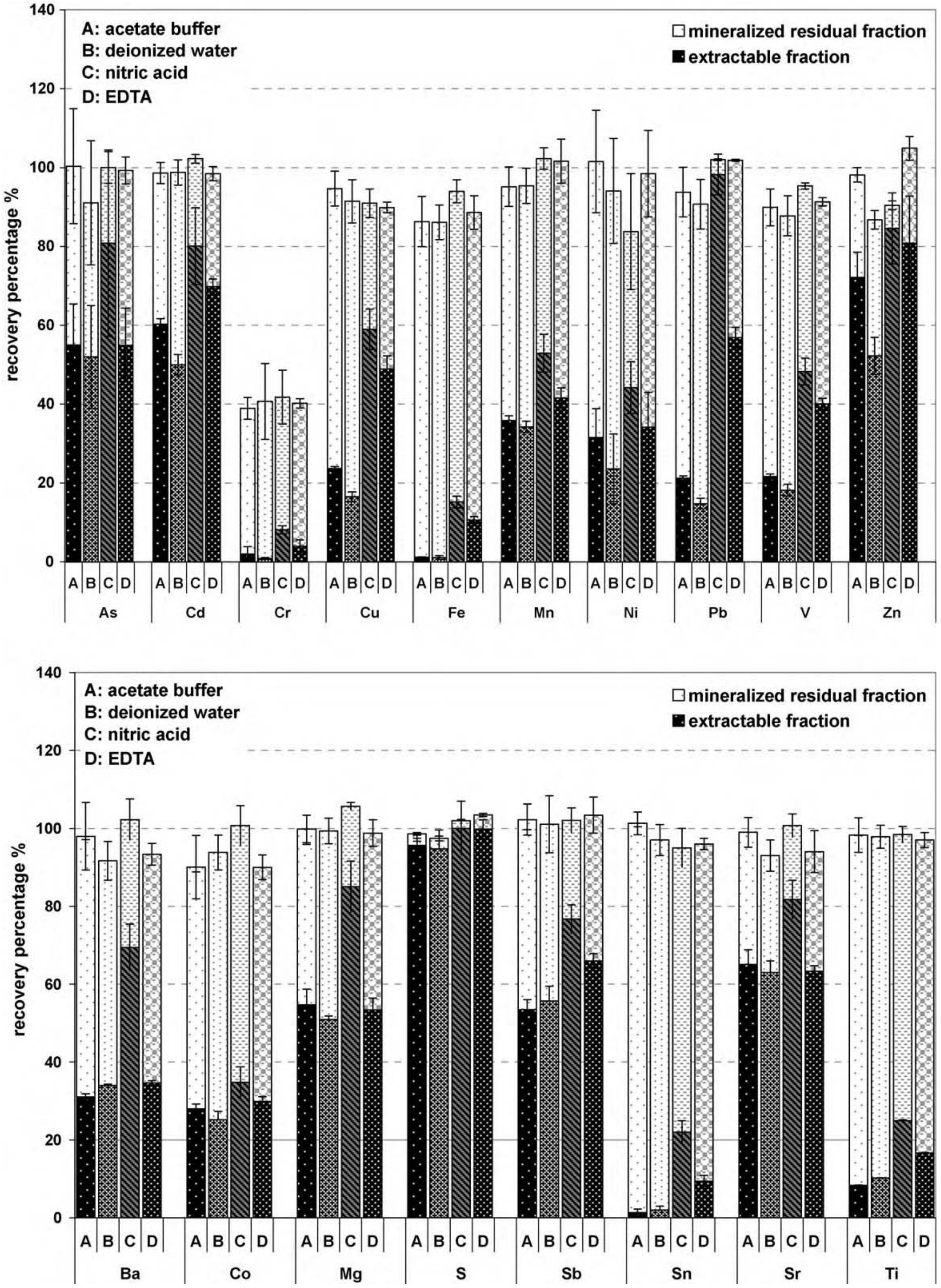

Fig. 1. Recovery percentages of the two fractions, extractable and mineralized residual, adopting different extracting solutions, estimated vs. certified values (NIST 1648; upper panel), or vs. total concentration measured by direct acidic digestion of the sample (lower panel). Error bars were calculated from six replicates and include interdiurnal variability.

efficiencies comparisons. It can be noticed a general increase of real samples standard deviations (SD) with respect to reference material. It is worth noting that SD in real samples, besides analytical repeatability, also suffers of the natural variability of PM composition, which results in a different distribution of elements between the extractable and mineralized fractions, as it will be better discussed in the following sections. Nevertheless, the mean values of extractable percentages are comparable with those obtained on reference material for all elements, with the exception of Cd, V and Cu, that show higher extraction percentages in real samples. These differences can be explained on the basis of: (i) different samples chemical composition drawn in various times and places

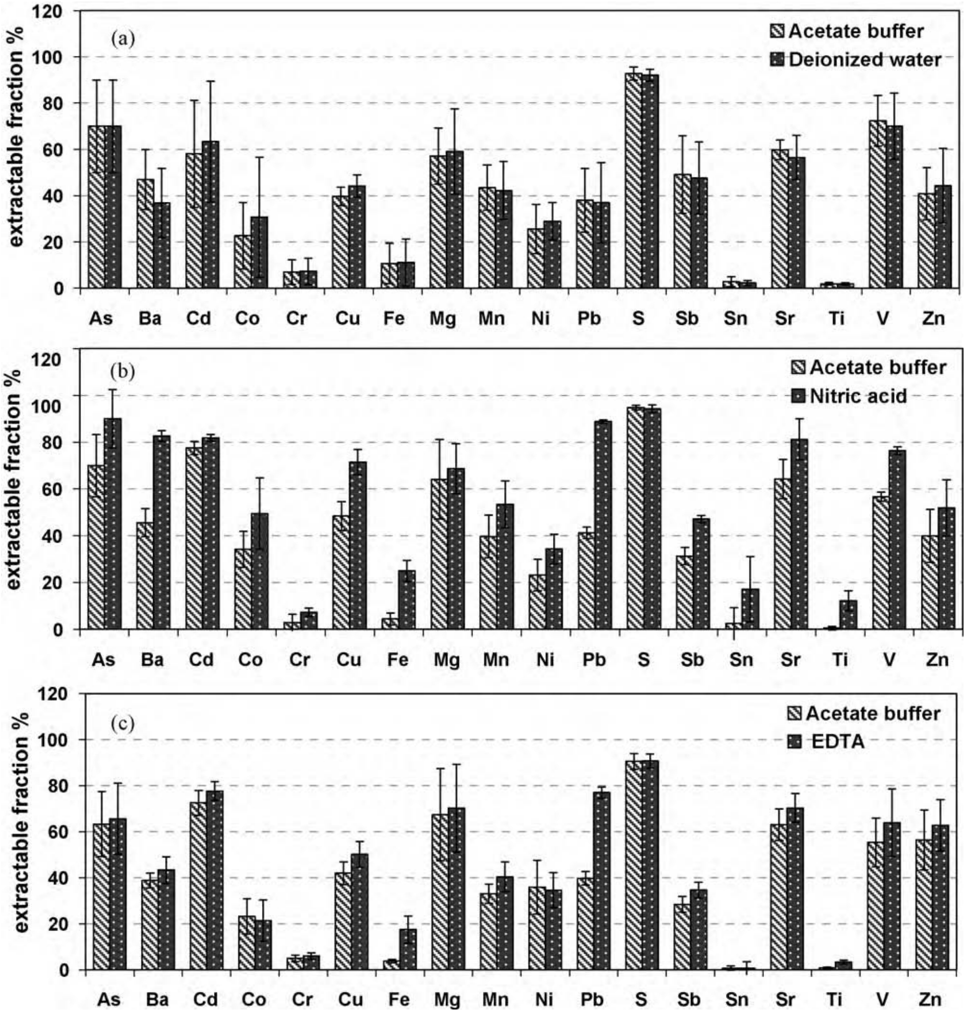

Fig. 2. Mean values and variability (standard deviation) of extractable fraction percentage (extractable fraction concentration/total concentration × 100) obtained for PM_{10} samples pairs: (a) comparison between A and B solutions (6 samples); (b) comparison between A and C solutions (14 samples); (c) comparison between A and D solutions (14 samples).

and (ii) particles with aerodynamic diameter (AD) > 10 μm that are present in NIST, but that are excluded from sampling during PM_{10} collection.

3.2.1. Water extraction

Deionized water (solution B) is probably the most widely used extractant solution for PM elemental solubility evaluation [4,17,28,34–38,40]. Fig. 2a shows that, according to data obtained on reference material, the extraction efficiency of the two solutions is totally comparable. However, analyzing in great detail results of each pair, significant differences, among values obtained for the various pairs analyzed (Cu, Pb, Fe, Ba and, less evident, Ni, V, Cr and Sr), were noticed. In Fig. 3, differences among the amounts extracted in water and in acetate buffer for each of the analyzed samples pair are reported. It can be pointed out that the water extractable fraction of these elements is affected by spontaneous pH changes of the solution (left axis), and by the concentration of extracted sulphate (right axis). This dependence of the extraction efficiency from PM intrinsic acidity, has the advantage to reflect the natural environmental variability (water extraction is more representative of environmental behaviour of elements); in our opinion it constitutes a serious drawback to the use of fractionation methods for improving emission sources traceability. In fact, water extractable concentrations do not only depend on chemical composition of primary particles emitted by PM sources, but also on concentration of ammonium sulphate and nitrate, secondary species (independent sources) main responsible for changes in spontaneous pH of PM [34,39,40,56].

3.2.2. Nitric acid extraction

Results obtained by comparing the extracting efficiency of acid nitric 0.200 M with acetate buffer in PM_{10} samples are reported in

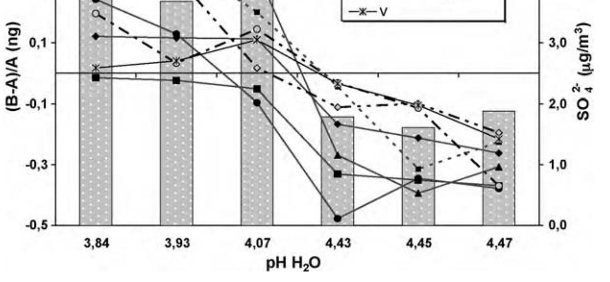

Fig. 3. Normalized variation of extracted amount in H_2O relative to extracted amount in acetate buffer and links (connections) with spontaneous pH of solution and sulphate concentration (secondary axis).

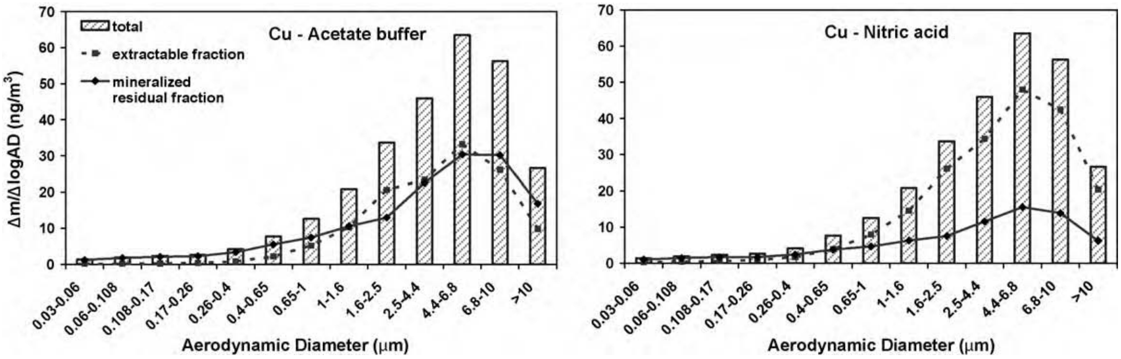

Fig. 4. Comparison between extractive efficiency (Cu) of acetate buffer and nitric acid on size-segregated samples.

Fig. 2b. As expected, the extracting efficiency in HNO_3 is markedly higher than the acetate buffer one for almost all elements.

Results of size-segregated samples were examined as to understand how this higher extraction efficiency could be reflected on the use of chemical fractionation data for source apportionment studies. Due to the well-known relationship between physical and chemical processes of particle formation and particle aerodynamic diameters (AD) [6,28,32,42,57], size-segregated sampling produces useful information about PM sources. In particular, stages 1–9 of the impactor collect fine particles (0.03 μm < AD < 2.5 μm; $PM_{2.5}$), mainly generated by high temperature processes such as combustion, while stages 10–12 collect coarse particles (2.5 μm < AD < 10 μm; $PM_{(10-2.5)}$), mainly produced by mechanical processes (i.e. abrasion or re-suspension). The combination of chemical and dimensional fractionation is then an efficient tool for evaluating chemical fractionation selectivity [43]; essentially, the more differ dimensional distributions of chemical fractions are, more selective the extractive procedure will be.

Size-resolved results about Cu analysis are given in Fig. 4. Cu is nearly exclusively present in coarse particles. In that case, extractable and mineralized residual fractions have the same dimensional distribution (with the difference that nitric acid shows a major extractive efficiency that acetate buffer) and chemical fractionation does not seem to significantly improve the elemental analysis selectivity. For Zn, Ti, Sr, Fe and Ba, the situation is similar to Cu and in other cases (Ni, Mn, Mg, Co, S) little differences in dimensional trends of the two fractions, quite difficult to elucidate, can be pointed out. However, some elements (As, Pb, Sb, Sn and V) present very different dimensional distributions in the extractable and mineralized residual fractions (Fig. 5), and chemical fractionation may be useful for refining source traceability. On Fig. 5, it can be noticed that when extracting with acetate buffer (column on the left) the extractable fraction is almost exclusively (>85%) associated with particles present in stages 1–9, while the mineralized residual consists of a great coarse component (percentages in stages 10–12, varying from 42% for Pb to 80% for As). Under these conditions, the extractable fraction could be adopted to trace elemental sources that produce fine particles, differentiating them from those producing coarse ones [43,44]. For all the elements in Fig. 5, nitric acid extraction (column on the right) involves a relevant concentration increase in the extractable fraction also from coarse particles. Therefore, HNO_3 use implies an extreme displacement of chemical fractionation towards the extractable fraction and it generates an unsought reduction of its selectivity towards classes of emission sources having different dimensional characterization.

It has to be remarked that for the elements reported on Fig. 5, the capacity to discriminate contributes from different emission sources has a particular environmental and toxicological interest. In fact, among those, As and Pb ambient air concentrations are regulated by the European Guideline 2004/107/CE because of their

Table 4
Pearson correlation matrices corresponding to data of PM_{10} mineralized residual fraction (period February 17 to March 2); comparison between acetate buffer (top) and EDTA (down) extractions. In bold values ≥0.70.

Mineralized residual fraction (EDTA)

Mineralized residual fraction (acetate buffer)

	As	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	S	Sb	Sn	Sr	Ti	V	Zn
As	1,00	-0,31	-0,43	-0,25	-0,34	-0,31	-0,19	-0,31	-0,16	-0,58	-0,48	-0,11	-0,21	-0,06	-0,44	-0,40	-0,02	0,13
Ba	-0,29	1,00	**0,78**	**0,73**	**0,83**	**0,97**	**0,98**	**0,84**	0,35	**0,70**	**0,91**	**0,85**	**0,95**	**0,96**	**0,95**	**0,94**	**0,71**	-0,41
Cd	-0,47	**0,70**	1,00	**0,87**	0,58	**0,84**	**0,74**	0,48	0,10	0,57	**0,92**	0,64	**0,86**	**0,78**	**0,74**	0,58	0,43	-0,25
Co	-0,21	**0,77**	**0,81**	1,00	0,66	**0,81**	0,66	0,56	-0,29	0,36	**0,87**	0,67	**0,86**	**0,77**	**0,77**	0,60	0,15	-0,14
Cr	-0,19	**0,85**	0,58	0,60	1,00	**0,89**	**0,79**	**0,94**	0,18	**0,81**	**0,83**	**0,82**	**0,84**	**0,75**	**0,85**	**0,90**	0,44	-0,24
Cu	-0,73	0,46	**0,81**	0,42	0,54	1,00	**0,96**	**0,84**	0,27	**0,75**	**0,96**	**0,86**	**0,99**	**0,95**	**0,92**	**0,90**	0,64	-0,37
Fe	-0,18	**0,92**	**0,74**	**0,73**	0,67	0,38	1,00	**0,80**	0,46	**0,70**	**0,86**	**0,84**	**0,94**	**0,97**	**0,87**	**0,89**	**0,81**	-0,46
Mg	0,20	**0,83**	0,32	0,52	**0,78**	0,00	**0,80**	1,00	0,29	**0,76**	**0,73**	**0,90**	**0,78**	**0,74**	**0,90**	**0,95**	0,52	-0,09
Mn	0,39	0,07	-0,02	-0,22	-0,12	-0,20	0,33	0,24	1,00	0,60	0,14	0,29	0,18	0,27	0,21	0,33	**0,86**	-0,24
Ni	-0,52	-0,35	0,02	-0,34	-0,06	0,57	-0,53	-0,64	-0,40	1,00	**0,73**	0,65	0,65	0,56	0,68	**0,74**	0,62	-0,24
Pb	-0,45	**0,78**	**0,92**	**0,74**	**0,83**	**0,86**	0,69	0,46	-0,13	0,16	1,00	**0,73**	**0,94**	**0,86**	**0,88**	**0,81**	0,47	-0,39
S	-0,24	0,63	**0,90**	**0,86**	0,44	0,53	**0,76**	0,39	-0,02	-0,29	**0,74**	1,00	**0,86**	**0,84**	**0,89**	**0,82**	0,62	0,08
Sb	-0,35	**0,81**	**0,95**	**0,89**	0,66	0,64	**0,86**	0,54	-0,03	-0,24	**0,87**	**0,96**	1,00	**0,97**	**0,90**	**0,84**	0,60	-0,33
Sn	-0,38	**0,75**	**0,87**	**0,86**	0,45	0,49	**0,86**	0,47	0,03	-0,38	**0,70**	**0,94**	**0,95**	1,00	**0,86**	**0,83**	**0,71**	-0,41
Sr	0,14	**0,79**	0,24	0,43	**0,86**	0,10	0,61	**0,90**	0,13	-0,35	0,49	0,15	0,38	0,23	1,00	**0,95**	0,53	-0,17
Ti	0,03	**0,93**	0,47	0,66	**0,78**	0,13	**0,90**	**0,97**	0,23	-0,63	0,55	0,51	0,67	0,63	**0,86**	1,00	0,60	-0,34
V	-0,15	0,60	**0,75**	0,47	0,36	0,47	**0,83**	0,44	0,61	-0,31	0,60	**0,73**	**0,75**	**0,75**	0,24	0,55	1,00	-0,37
Zn	0,12	-0,56	-0,29	-0,34	-0,11	0,08	-0,76	-0,53	-0,52	**0,71**	-0,10	-0,42	-0,45	-0,65	-0,25	-0,65	-0,65	1,00

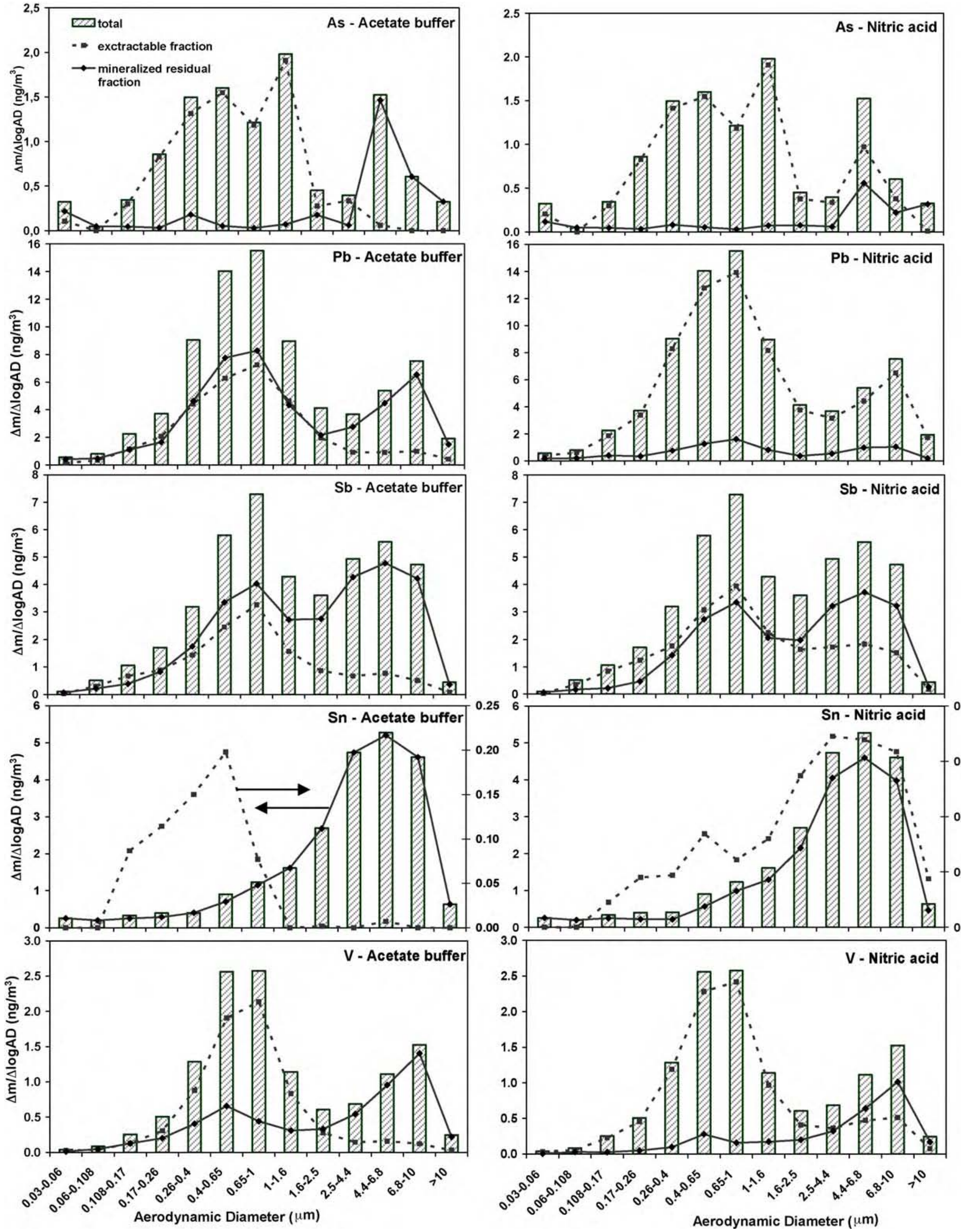

Fig. 5. Comparison between extractive efficiency (As, Pb, Sb, Sn and V) of acetate buffer and nitric acid on size-segregated samples.

health effect; Sb results to be an emerging environmental problem [58–61], due to its concentration increase in urban air, that was registered in the last years, and V is frequently adopted, as tracer for environmental impact coming from discharges of oil bearing plants. In previous samplings [43], Cd, included in the European Guideline 2004/107/CE too, has shown a similar behaviour to As, Pb, Sb, Sn and V, but, during the sampling period related to these comparisons, it was almost completely found in fine fraction (ca. 90% of total Cd in particles with AD < 2.5 μm); for this reason, it was not possible to compare extractant selectivities for this element.

3.2.3. EDTA extraction

Results concerning the comparison between extraction efficiency of EDTA solution and acetate buffer on PM_{10} samples are reported in Fig. 2c. It can be noticed that, with the exception of Pb, EDTA involves small changes of extractable fraction relative to

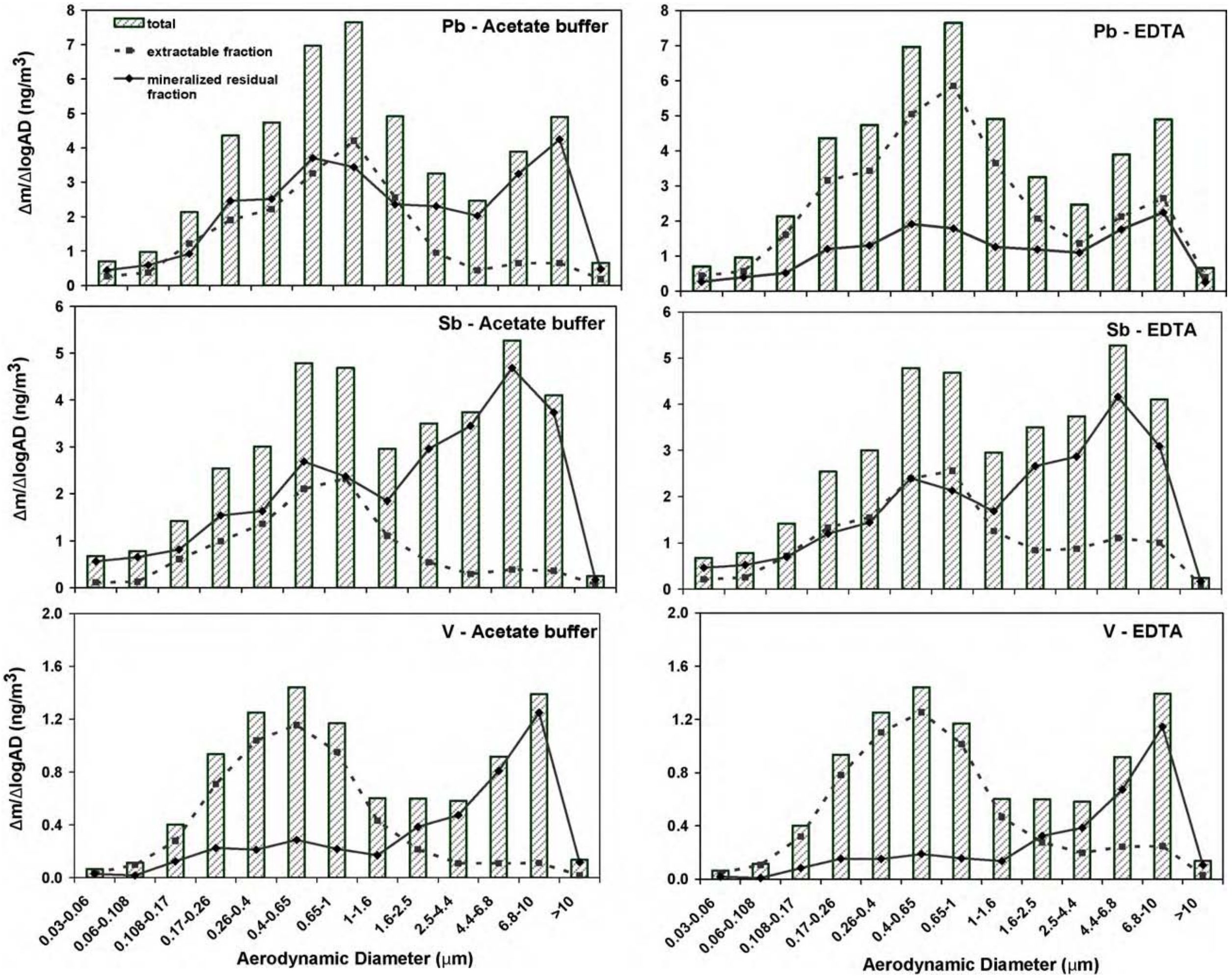

Fig. 6. Comparison between extractive efficiency (Pb, Sb and V) of acetate buffer and EDTA on size-segregated samples.

acetate buffer one. Extraction efficiency differences totally comply with the reference material ones, even if they are smaller for Cd, Cu and V. As previously done for the comparison between acetate buffer and nitric acid, some considerations on chemical fractionation selectivity can be done, examining size-segregated samples results. Dimensional behaviour of the two extractant solutions essentially results equivalent for all elements, except for Pb, Sb and V (Fig. 6). In case of Pb it can be pointed out that alteration of chemical fractionation is rather remarkable and involves, as yet discussed for HNO_3, a lower selectivity of the EDTA extraction, related to the acetate buffer one. Similarly, it can be noticed how differences of extraction efficiency for Sb and V, though of small extent, mainly concern coarse fraction, involving also in this case a reduction of fractionation procedure selectivity. On the basis of obtained results, EDTA adoption does not seem to have particular advantages in comparison to the acetate buffer one.

3.2.4. Acetate buffer extraction

Results relative to acetate buffer use have been already widely described in the previous sections; nevertheless, when comparing two different sampling periods, whose data are reported in Figs. 2, 5 and 6, some considerations on the behaviour of chemical fractionation can be done. The PM elemental concentrations are notably lower for January sampling (Figs. 2b and 5) than for February–March one (Figs. 2c and 6). This high time-variability is characteristic for all air pollutants and is mainly driven by the dilution properties of low atmosphere [62,63]. As above discussed, in both cases, the extractable fraction of As, Cd, Sb, Pb, Sn and V is almost exclusively present in fine particles and the acetate buffer extraction of PM_{10} samples allows tracing, in a selective way, contribution from sources responsible of fine particles emission, potentially more dangerous for human health [9,10] and prevalently of anthropic origin. However, during the second period, a slight decrease of the mean percentages of extractable fraction was noted for some elements (Fig. 2b vs. c): Pb 41% vs. 39%; Sb 31% vs. 28%; V 56% vs. 54%). Size-segregated sample analysis (Fig. 5 vs. Fig. 6) shows that this variation is due to a greater relative impact of sources responsible for coarse particles emission ($PM_{(10-2.5)}/PM_{2.5}$ ratio is higher in the second sampling).

Since acetate buffer extraction seems to offer the advantage of a better selectivity towards PM sources, further tests were done for evaluating extraction procedure robustness towards variation of chloride ion concentration and aging effects.

Chloride ion concentration in PM increases significantly during sea-spray transport events and in a previous monitoring campaign [64], it was showed an important raise in extractable concentrations of some elements in presence of sea aerosol transport events; that was explainable either as a co-transport of anthropic type dusts, or like an increase of elemental solubility, due to complexation equilibria with Cl^-. Therefore, some comparison trials between extractable concentrations in presence of growing additions of Cl^- (from 0 to 50 mg/L NaCl) were carried out, both concerning reference material and PM_{10} equivalent pairs. The observed differences were always lower than analytical repeatability of the procedure, showing that fractionation was not changed in presence of Cl^-.

Moreover, tests for evaluating aging effect of dust on elemental solubility were executed. Similarly, significant differences for the obtained extractable percentages were not checked both on reference material after heating cycles at 105 °C, and on PM_{10} samples subsequently to prolonged exposure to weather factors.

3.3. Time patterns

Generally, source apportionment studies are based on the analysis of chemical tracer covariance [45]. Even if the number of samples utilized in this study do not permit a proper statistical treatment, some information can be obtained by evaluating temporal trends and, in particular, estimating the Pearson correlation matrices for the extractable and mineralized residual fraction [27,43]. Generally, high values of correlation coefficients between two elements indicate that the prevalent source is common to both elements and that they can be then considered as selective traces for that source. In compliance with previous considerations, the best correlations were achieved using acetate buffer and EDTA as extracting solution. For these solutions, correlation matrices were significantly different for the extractable and mineralized residual fraction; this confirmed good selectivity of chemical fractionation method in comparison to distinct classes of emission sources.

In accordance to previous studies [43,44], most elements in the mineralized residual fraction show great correlation values, as their prevalent source in urban air is the re-suspension of road dust. As shown in Table 4, correlation values are well higher after acetate buffer extraction, confirming this solution good reliability to trace non-exhaustive traffic contribution by chemical fractionation methods.

4. Conclusions

It has been presented a critical evaluation of H_2O, HNO_3, acetate buffer and EDTA performances as extracting solutions in elemental chemical fractionation of PM, based on the extractable percentages comparison and on fractions selectivity towards some classes of sources with a different dimensional characterization. This comparison could be a useful tool for comparing studies of elemental solubility, reported in literature, which refer to meteoclimatic and geological diverse situations.

The usage of a combined chemical and dimensional fractionation resulted particularly helpful for evaluating the extracting methods selectivity. In fact, it was possible to interpret the extraction efficiencies variations by comparing the behaviour of extracting solutions on size-segregated samples, referring to the different dimensional characterization of PM sources.

Even if it is evident that it does not exist a “perfect” extracting solution, some considerations on the advantages and disadvantages offered by different extracting methods could be made.

Deionized H_2O extraction, the most frequently adopted in literature studies, has the advantage of being more representative of the interactions of elements with environmental and biological matrices; nevertheless, it is less indicated for source apportionment studies, as the extracted concentrations efficiency depends on spontaneous pH of the analyzed matrix, giving variable results, upon the content in secondary species, as ammonium sulphate.

HNO_3 permits a good control of adsorption phenomena and buffers pH variation, but strongly overvalues bioavailability and mobility estimation; furthermore, with respect to acetate buffer, it leads to a less selectivity regarding emission sources, particularly observed for As, Pb, Sb, Sn and V, elements of great environmental interest. However, the adoption of this solution could be advantageous for determining pseudo-total content of elements, involving less time with respect to those necessary for performing microwave assisted acidic digestion.

EDTA and acetate buffer show a similar behaviour; even if EDTA is able to guarantee a good robustness concerning the presence of complexing species, it results less selective than acetate buffer for Pb, Sb and V.

As seen in this work, mild extraction in acetate buffer seems to establish the best compromise between method selectivity and robustness.

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