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Determination of metals, metalloids and non-volatile ions in airborne particulate matter by a new two-step sequential leaching procedure

Part B: Validation on equivalent real samples

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Abstract

Due to the lack of proper standard materials for airborne particulate matter collected on filters, a validation scheme was developed, which is here described, to the aim of testing the application of leaching procedures performing both ions and elemental determinations on real samples of airborne particulate matter collected on filters. The scheme has been developed on a two-step leaching method (extraction in acetate buffer and acid dissolution of residue) previously developed by authors and consists of two series of tests to be run on *n* pairs of equivalent parallel samples filter-collected. The first series of tests aims to assess on real samples the equivalence between results obtained by the tested procedure with those obtained by the EMEP ions extraction and the EN 12341 standard methods, whereas the second aims to evaluate the reproducibility of analytical results of elemental determination in the leached and dissolved fractions; in the latter case data reliability is also evaluated as a function of the environment-intrinsic variability of real samples.

To avoid errors due to sampling differences data from filter pairs were standardized both by gravimetric determination of loaded filters, according to the EN 12341 standard and by the rate $[SO_4{}^{2-}]_A/[SO_4{}^{2-}]_B$, where $[SO_4{}^{2-}]$ indicate the soluble sulphate concentration in the extract; in the latter case values improved for all elements and in both fractions. Results of equivalence with standard methods and reproducibility tests are evaluated as mean relative percentage differences ($\Delta\%$) and percentage elements recoveries ($R\%$). The application of the validation scheme to the two-step leaching method is here discussed for non-volatile ions and for 17 elements detected on 22 pairs of low-volume collected PM_{10} samples on Teflon filters.

Keywords: Particulate matter; Sequential leaching procedure; Elemental analysis; Soluble ions analysis; Validation

1. Introduction

A new two-step sequential leaching method was developed for airborne particulate matter (PM), that is described in a previous work by the same authors [1], based on a single extraction in acetate buffer, where extracted non-volatile ions and elements are determined, respectively, by ions chromatography (IC) and inductively coupled plasma optical emission spectroscopy (ICP-OES), followed by ICP-OES elemental determination of the residue mineralized by acid digestion [2].

A microanalytical approach was applied, having as target small PM amounts collected on Teflon filters that are commonly get by 24 h low-volume sampling, for routine application to large scale monitoring of ambient air.

The new procedure was assessed for equivalence with the reference methods for ions extraction [3] and for elemental determination of PM_{10} [4] by using the reference material NIST 1648 coarse urban dust. Results were encouraging both for ions extraction and for the recovery efficiencies of almost all metals certified on NIST 1648 SRM.

Although the NIST 1648 coarse urban dust was the most appropriate SRM for the scopes of the previous work, when the two-step method was developed, its use presents some limitations when the purpose is to validate a leaching method on real samples of filter-collected PM_{10} or smaller size particulates. Indeed, the coarse nature of NIST 1648 implies differences in chemical composition and physical behaviour with respect to fine and ultrafine PM fractions; moreover this SRM is not

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filter-loaded, whereas the filter support could affect extraction efficiencies either by filter blank or by eventually keeping a portion of the collected particulate entrapped in the pores. Also, at present, reference materials for airborne particulate collected on filters are scarcely available. Other authors report the use of alternative reference materials, e.g. the NIST 1640 trace elements in natural waters [5], the NIST 1633b pulverized coal [6], the BCR 76 city waste incineration ashes [7] and other standards; however the suitability of these SRMs is as arguable as for NIST 1648 in representing the physico-chemical behaviour of a particulate collected on filter at urban or background sites. Also, the NIST 2783 SRM [8,9], which was recently commercialised and is certified for $PM_{2.5}$ deposited on polycarbonate filters [8] is not suitable to the purpose of validating leaching procedures using aqueous solvents. Indeed, besides the high cost of this SRM, the deposition of the particulate on the filters membrane is obtained by means of a suspension of the $PM_{2.5}$ particles in deionised water, which can consequently induce partial removal of the hydrosoluble fraction of ions and metals. Following these considerations, a validation scheme has been developed in this work, which allows to properly test a leaching procedure in which both ions and elemental determinations are performed for application to real samples of airborne particulate matter [1].

The scheme is based on the use of equivalent filter pairs and consists of two series of tests, the first aimed to assess on real samples the equivalence of results obtained by the tested procedure with the EMEP ions extraction [3] and the EN 12341 [4] standard methods and the second aimed to evaluate the reproducibility of analytical results of metals determination in both extract and mineralized residue fractions. A number of 22 twins PM_{10} samples were collected in parallel on Teflon filters at the site of the Institute for Atmospheric Pollution of the National Research Council of Italy (CNR) by two impactors certified for equivalence by the Institute [10].

The choice of using twin filters instead of filter cutting was made considering both the drawbacks which could arise from a likely inhomogeneous distribution of particulate on the support [9] and the fact that cutting filters loaded with small amounts of PM mass, 1–2 mg or less typically obtained by low-volume 24 h sampling, would severely affect the analytical uncertainty of results. Furthermore, Teflon filters used in this work to the aim of minimizing the contribution of blanks are ring-supported, whose cutting can induce, at any rate, large errors. Nevertheless, also in the case of twin filters collected by equivalent samplers possible errors have to be taken into account, e.g. in the gravimetric determination of such small filter-collected PM masses.

The suitability of soluble sulphate determination as parameter to assess the equivalence of air particulate sampling was recently demonstrated [10]. Therefore, masses of twin filters were evaluated by both sampling equivalence criteria, the gravimetric determination and the determination of soluble sulphate ion in the extract. Results of application of the validation scheme to the previously developed two-step method, as well as of the comparison between the two criteria of sampling equivalence, are discussed for non-volatile ions and 17 elements.

2. Experimental

2.1. Reagents

The following reagents have been used: deionised H_2O (Milli-Q), HNO_3 (65%, RPE, Carlo Erba, Rome, Italy), H_2O_2 (30%, Suprapur, Merck), glacial CH_3COOH (Carlo Erba), CH_3COOK (p.a. Sigma), Ion Chromatography (IC) and Inductively Coupled Plasma (ICP) standards (Merck).

2.2. Sampling of PM_{10} loaded filter pairs

During the sampling period from 31/01/2003 to 22/02/2003 22 pairs of twin filters were collected on Teflon membrane filters (47 mm diameter, 1 μm pore size, Gelman) at about 1.5 m above the ground level by in parallel working of two Sequair 92A (DAS, Italy). The mass of collected particulate was gravimetrically determined by weighting the Teflon filters, after conditioning for 48 h at relative humidity of 50% and $T = 22\,°C$, before and after sampling, by a micro-analytical balance GIBERTINI E 505 (sensitivity 0.01 mg). Sampled filters were put into separate containers, stored at 5 °C and in the absence of light and analyzed within a few days.

2.3. Analytical procedure

The two-step sequential leaching procedure, which was developed in a previous work [1], is here applied to real Teflon filter-collected PM_{10} samples after removal of the ring supporting the Teflon filter. Operative conditions related to the leaching procedure and to ion and elemental analysis were not modified.

The procedure has been run on unexposed filters in the same way as on the loaded filters. The blank was a reagent + vessel and laboratory-glass + filter blank and the values have been subtracted from the ICP-OES measurements. Blanks for all metals were lower than 30% of measured values.

S and Mg in the extract fraction were determined by both chromatographic (as sulphate and Mg^{2+}, respectively) and ICP-OES techniques, to the purpose of providing an internal check of data quality. Differences within the experimental error were always observed.

The sampled twins filters were analyzed by random sequence.

3. Results and discussion

The validation scheme developed in this work consists of two series of tests. The first series aims to assess on real samples the equivalence of results obtained by the tested leaching procedure with those obtained by applying standards methods, that are the EMEP reference method for water extraction of ions [3] and the EN 12341 standard for the recovery of metals from total dissolution of PM_{10} [4]. The second series of tests is then performed to evaluate the reproducibility of analytical results of metals determination in both extract and mineralized residue fractions. Application of the validation scheme to the previously developed two-step leaching method [1] is hereafter discussed.

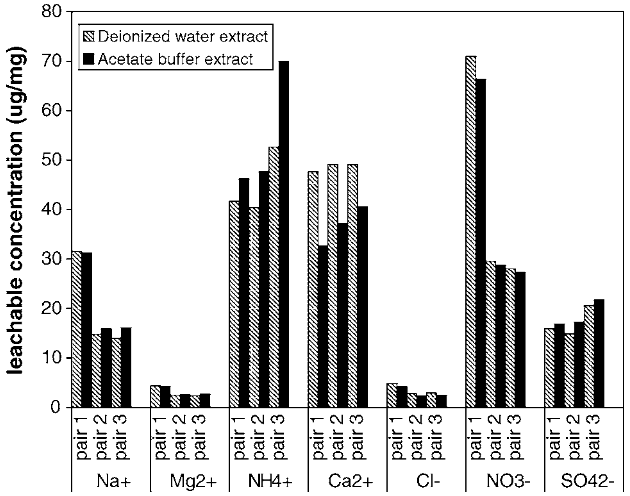

Fig. 1. Ions analysis: comparison on twins real samples of the results obtained by deionised water [3] extraction with those obtained by acetate extraction; results are reported for six filter pairs.

3.1. Equivalence with reference procedures

The first series of tests was carried on the collected twins samples to assess the equivalence of the new procedure. For these tests, we used six pairs of sampled filters for the ionic analysis and other six for the elemental analysis, loaded with PM$_{10}$ masses ranging from 1 to 2 mg.

For ionic analysis, the equivalence of the leaching procedure was tested by extracting six pairs of twins filters, one member in deionised water [3] and the other in the acetate buffer.

In the case of elemental determination, for each pair of twins filters the following protocol has been followed: one twin was treated by the tested procedure and the concentrations of each metal in the two fractions (extract and mineralized residue) were added up and compared with the total metal concentration obtained by direct dissolution of the corresponding other twin [2].

In these tests, the equivalence of loaded twins filters was checked by gravimetric determination and data were mass-normalized to compensate errors due to the parallel sampling.

3.1.1. Ionic analysis

The results obtained for extracted non-volatile ions are reported in Fig. 1 for six pairs of twin filters. The extraction in acetate buffer gave results largely similar to those obtained with deionised water. Differences of about 10%, which are comparable to the R.S.D. values found with both considered methods, are observed for Na^+, Mg^{2+}, Cl^-, $NO_3{}^{2-}$ and $SO_4{}^{2-}$, confirming the results previously obtained on NIST 1648 [1]. For Ca^{2+} and $NH_4{}^+$ differences of about 20% were found between the two methods. For these two ions, a small disagreement between extraction values obtained from twins samples was already noted in previous studies [10], which was ascribed to sampling operations rather than to analytical errors.

The size distribution curve of Ca^{2+} ion in particulate matter, indeed, presents a steep slope in correspondence of a.d. 10 μm, so that even small differences in the cut-off of the inlet impactors may cause large differences in Ca^{2+} ion content and may induce large sampling errors.

Table 1
Recovery percentages obtained by the two-step sequential procedure (as sum of the two fractions) with respect to the direct acid digestion

Element	*R%*	Element	*R%*
Al	61 ± 6	Pb	108 ± 7
Cd	103 ± 10	S	101 ± 2
Cr	113 ± 10	Sb	96 ± 7
Cu	94 ± 4	Se	105 ± 22
Fe	88 ± 1	Si	103 ± 13
Mg	93 ± 4	Ti	99 ± 8
Mn	96 ± 5	V	103 ± 2
Ni	93 ± 5	Zn	96 ± 15

Values obtained as average of six filter pairs.

Ammonium nitrate is involved in evaporation equilibria and the uncertainty of results is affected by evaporation, giving problems of losses due to small temperature differences in the heated inlets during sampling.

All observed differences, however, are well below the great variability usually observed for the ions concentration of extracts from real loaded filters; therefore the extraction step of the tested procedure could be considered equivalent to the ions extraction reference method.

3.1.2. Elemental analysis

In Fig. 2, the results obtained for elemental analysis are reported for six twin pairs of PM$_{10}$ samples. Table 1 also reports for clarity the mean and S.D. of total metal percentage recoveries, obtained as sum of concentrations in the extract and in the mineralized residue and indicated as $R\%$ [$R\% = ((\text{extract} + \text{residue})/\text{direct dissolution}) \times 100$], with respect to the total metal content obtained by direct dissolution. Data on As are not reported since values in the residue fraction were in the examined samples below the quantification limits (LOQ) of the method [1].

For all metals, with the exception of Al, results from the application of the tested procedure are largely comparable with those by direct dissolution, confirming that the requirements of accuracy of the procedure are respected also in the treatment of field samples. The far lower total recovery of Al obtained with the tested method with respect to direct dissolution can be addressed, as yet discussed for the application on NIST 1648 [6], to the presence of insoluble Al oxides. Incomplete recoveries by both the compared methods are expected [6] also for Cr and Si, and could account for the higher values of related standard deviations. Despite the results obtained on NIST 1648, recoveries of Zn show greater variability than for other metals. This could be likely due to high blanks of Zn, which is present in high concentrations in the supporting ring of Teflon filters.

Data related to Cd and Se too are affected by a larger error than for other elements, due to their small total content in the collected samples and to the fact that measured values are close to their LODs (see ref. [1]).

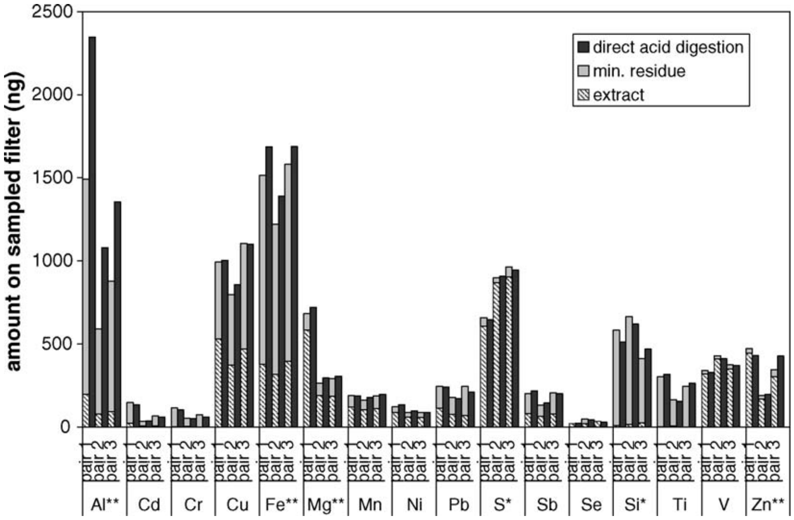

Fig. 2. Elemental analysis: comparison on twins real samples of the results obtained by direct acid digestion [2] with those obtained by the proposed sequential procedure; results are reported for six filter pairs. (⋆) Values divided by 100; (⋆⋆) values divided by 10.

3.2. Reproducibility of elemental analysis

The second series of tests was performed on 10 twin pairs. Both filters (A and B) of each pair are treated with the two-step method, to evaluate the reproducibility of analytical results of element determination in both extract and mineralized residue fractions.

The mean relative percentage differences (Δ%), reported in Table 2, are calculated as averages of the relative errors of each pair of A and B twin filters:

$$\Delta\%_{i,f} = \left(\frac{|m_{Ai,f} - m_{Bi,f}| \times 2}{(m_{Ai,f} + m_{Bi,f}) \times 100}\right)$$

where m_A and m_B are the masses of element i in the fraction f (extract e, mineralized residue r or sum of the two fractions t) measured, respectively, on the twins members A and B of each filter pair. Before calculating the $\Delta\%_{i,f}$ values, data were standardized to avoid errors due to sampling differences. As above mentioned, two different standardization procedures were applied, based on gravimetric determination of loaded filters according to the reference method for the assessment of sampling equivalence [4] or on determination of sulphate in the soluble fraction [10].

In the latter case, data from the twins pairs samples were normalized by the rate $[SO_4^{2-}]_A/[SO_4^{2-}]_B$, where $[SO_4^{2-}]$ indicate the sulphate concentration in the acetate extract.

The Δ% values improved for all elements and in both fractions when results were sulphate-standardized. This is explicable with the error associated to the mass determination on low-volume collected samples (ca. 4%), which is higher than that

Table 2
Reproducibility of results on twins samples

	Extract fraction		Min. residue fraction		Sum	
	Δ% sulphate	Δ% mass	Δ% sulphate	Δ% mass	Δ% sulphate	Δ% mass
Al	22	25	26	28	27	28
As	4	11	–	–	–	–
Cd	11	15	16	29	13	14
Cr	5	5	9	10	8	9
Cu	17	21	21	23	16	18
Fe	8	9	12	14	9	10
Mg	19	21	14	17	16	16
Mn	8	12	10	11	7	9
Ni	10	14	11	11	8	10
Pb	5	12	13	15	7	11
S	–	7	–	10	–	7
Sb	8	11	10	9	4	8
Se	12	13	–	–	–	–
Si	8	12	44	44	39	39
Ti	16	13	21	25	16	18
V	4	7	9	10	4	6
Zn	20	24	27	28	23	25

Δ% values (mean of 10 filter pairs) obtained after data normalization by soluble sulphate or by mass ($\Delta\%_{i,f} = (|m_{Ai,f} - m_{Bi,f}| \times 2/(m_{Ai,f} + m_{Bi,f})) \times 100$).

Table 3
Linear regression results ($m_{\mathrm{A}i,f} = am_{\mathrm{B}i,f} + c$) and variability ranges of twins samples

	Extract fraction				Mineralized residue fraction			
	R^2	a	c (ng)	Range (ng)	R^2	a	c (ng)	Range (ng)
Al	0.94	0.99	12.8	67–1784	0.98	0.94	213	512–22820
As	0.99	1.07	−2.8	14–160	–	–	–	n.d.
Cd	0.74	0.70	3.7	6–18	0.97	0.87	0.9	2–33
Cr	0.95	1.03	−1.0	9–30	0.91	1.18	−13	81–261
Cu	0.87	1.06	0.1	35–350	0.82	0.79	13.1	64–660
Fe	0.97	1.01	−164	253–7280	0.99	0.76	351	944–20896
Mg	0.95	0.98	30.4	192–4346	0.94	0.72	220	332–3136
Mn	0.98	0.97	2.7	37–308	0.98	0.80	8.4	24–223
Ni	0.62	0.74	12.7	17–76	0.90	0.89	13.6	42–188
Pb	0.99	1.12	−7.1	116–449	0.85	0.85	14.0	137–740
S*	0.92	0.74	13170	17150–153520	0.70	0.48	1693	2055–7333
Sb	0.98	1.04	0.3	14–100	0.99	0.93	0.4	6–132
Se	0.97	1.20	−4.0	6–53	–	–	–	n.d.
Si	1.00	0.99	−4.0	41–897	0.25	0.59	−4.5	128–4432
Ti	0.99	1.09	−1.8	5–40	0.99	1.19	1.0	9–878
V	0.99	1.03	−3.0	14–176	0.99	0.89	−146	7–77
Zn	0.04	0.40	1200	511–2620	0.68	1.18	0.0	417–5885

Results normalized by soluble sulphate.

* Results normalized by mass.

related to soluble sulphate determination (<2% both for chromatographic and for ICP-OES measurements) and thus affect the reproducibility of results. The improvement of $\Delta\%$ values gained by means of the soluble sulphate standardization confirms similar results found by previous studies and represents further evidence that the sulphate concentration can be conveniently used as tracer for equivalence-tests on low-volume samplers [10].

The acetate extraction of elements (Table 2) is highly reproducible for the major part of elements detected, since $\Delta\%_e$ values are below 10% even for elements, like As, Ni, V and Cr, whose concentration in the extracting solution is very low. Other trace elements, like Ti, Se and Cd, also show a good reproducibility, with $\Delta\%_e$ <20% despite their low concentration.

On the other hand, Al, Cu and Mg are in concentrations well above the quantification limits but show a $\Delta\%_e$ of about 20%. The reasons for these errors, which are much higher than those found in the previous application of the tested procedure to SRM [1], are not clear at present and further studies are being carried out to assess the possible influence of some sampling parameters (humidity and temperature in the sampling line or small differences in the particle cut-off of inlets). For Zn, as already observed for data reported in Table 1, the reproducibility of obtained results was severely affected by its high blanks, due to the Teflon filters supporting ring.

The observed general increase of $\Delta\%$ in the mineralized residue fraction was expected, due to the longer manipulation to which filters undergo during the second step to obtain this second fraction. Values of $\Delta\%$ related to As and Se are not reported here, as these metals are present in the considered samples mainly in the acetate extracted solution and were thus non-detectable in the mineralized residue fraction.

Si is poorly dissolved by HNO_3/H_2O_2 digestion, its residue fraction being then scarcely reproducible.

Al and Cr too are not quantitatively recovered by the acid digestion applied [1], but in the case of these two metals the mineralized residue fraction shows, particularly for Cr, an acceptable reproducibility. The $\Delta\%_r$ values of other elements are included in the range 10–15%, reaching the value of 20% only for Cd and Ti, whose concentrations in the samples were found very low.

It is worth noting that the relative errors $\Delta\%_t$, calculated on the sum of the concentrations in the two fractions, are generally lower than those related to each single fraction. This result indicates that small variations were in the extraction efficiency of the acetate solution, which were compensated when the total content was considered.

The reproducibility of the tested method is also assessed by calculating the linear regression between the twins filters (i.e. filter A versus filter B), with the aim of evaluating the data reliability also as a function of the environment-intrinsic variability of real samples. A linear equation

$$m_{\mathrm{A}i,f} = am_{\mathrm{B}i,f} + c$$

is used between the masses of each metal on the pairs of twins filters, where in the case of perfect equivalence the values $a = 1$ and $c = 0$ should be obtained. The regression parameters, reported in Table 3 for the extract and mineralized residue fractions, are strictly related to the broadness of the concentration ranges. Particularly, a good linearity was obtained for some metals, like Al and Mg in the extract fraction or Cd, Al and Ti in the residue, which showed fairly high $\Delta\%$ values, but present a scattered distribution of their amounts in the extracted filters.

In other cases, as Cd and Ni in the extract or Se in the mineralized residue, for which a low variability was noted, the regression parameters are scarce despite the low $\Delta\%$ values.

In Fig. 3, the average amounts of the elements found in the extract and residue fractions for each pair of filters ($(m_{\mathrm{A}i,f} + m_{\mathrm{B}i,f})/2$) are reported. The reported error bars correspond to the $\Delta_{i,f}$ value of each pair and allow the visualization

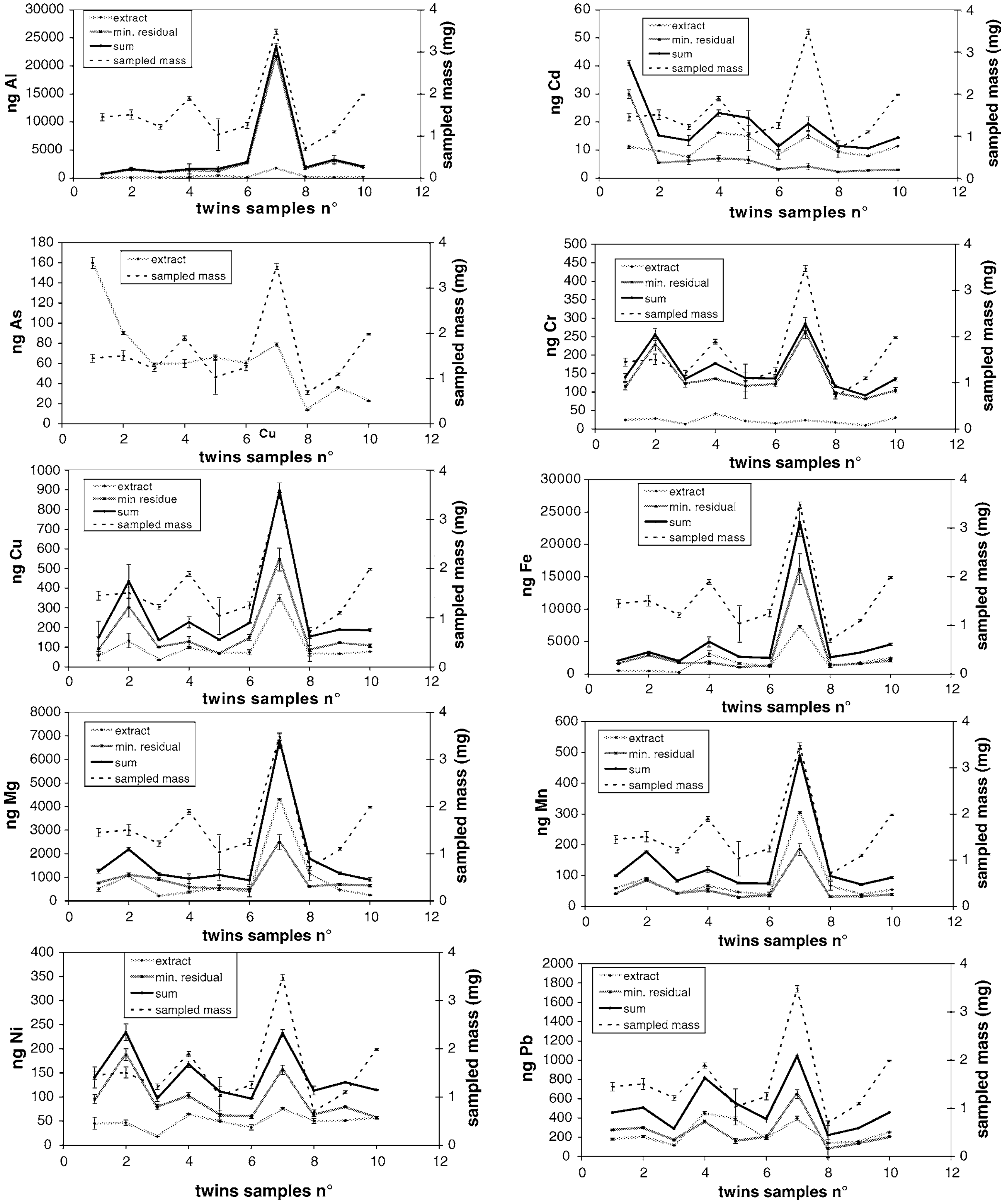

Fig. 3. Elements amount in the extract, mineralized residue and as sum of the two fractions for the twins samples analyzed. Sampled masses of PM_{10} are reported for comparison.

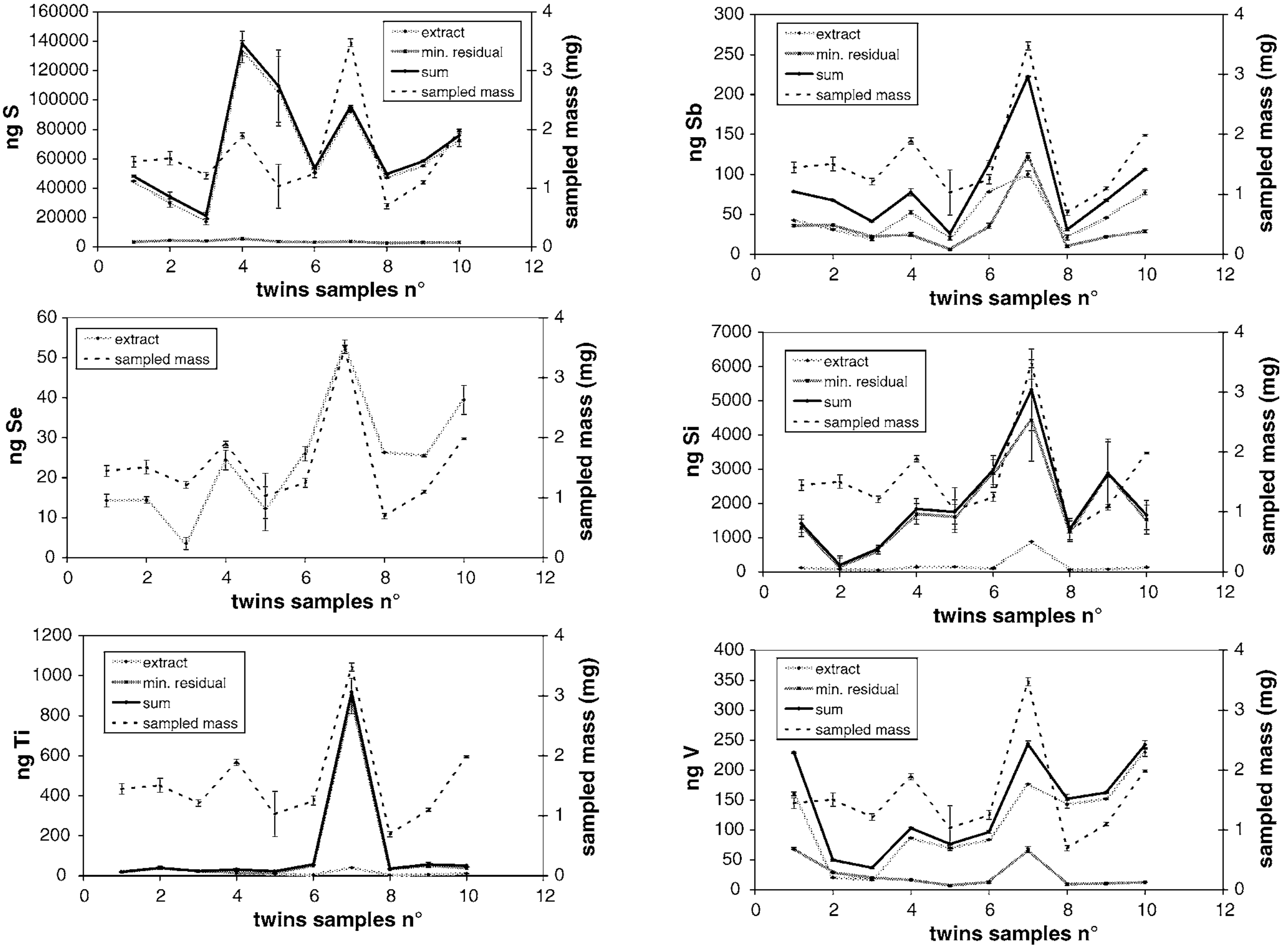

Fig. 3. (*Continued*).

of the reproducibility of results. The sampled masses of particulate are also reported for comparison. These first results provide a basis for at least two main future developments.

First, for almost all the elements the general trend of the extract fraction shows a good similarity with the total content. If confirmed by large-scale field applications of the tested analytical procedure, this result would allow the attainment of qualitative information on the behaviour of elemental content more easily and rapidly, by the sole analysis of the extract fraction that is a low-cost operation. A similar approach, based on the analysis of the elemental fraction soluble in water [5,11,12] or diluted acid solutions (HNO_3 [5,13] or HCl [14]), has been already proposed and fruitfully applied to various field studies [5,11,12,14–17] in which a good correlation of the extract content with the total content was found, mainly for non-crustal elements and ultrafine particles. The choice of using acetate buffer as extracting solution, however, despite it can be associated with lower extraction efficiency than by acidic solutions, offers good advantages of ensuring, on the same solution on which both ions and elemental analyses are performed, the equivalence of the non-volatile ions extracted with respect to the reference method [3] and the independence of the metals extraction efficiency from the specific acidity of the collected particulate (see ref.[1]).

A deeper examination of results in Fig. 3 shows some significant variations of the elemental distribution between the two fractions during the sampling period. For example, the extract fraction of V, Cd and Sb varies from 30 to 40% to more than 80% of the total, and for Ti and Fe a range from ca. 10 to 50% is observed. Of course, at present these results are far from having a defined environmental significance, as some important parameters which could influence the metals solubility, first of all the storage conditions of samples, still need to be carefully investigated. Nevertheless, it is largely predictable, also in agreement with results obtained by the application of other sequential leaching schemes [11,18–21], that the observed variations partly depend on the different emission sources affecting the sampling area and that the analysis of the elemental distribution between two fractions at different solubility could provide a powerful tool for their identification.

4. Conclusions

The proposed two-step sequential procedure is confirmed to be suitable for application on single low-volume collected real samples, with good analytical performances. This analytical approach allows two important goals to be reached. First, a wider chemical characterization (soluble ions and elements) may be obtained on a single sample together with a reduction of sampling costs and secondly a deeper knowledge of the behaviour of elemental content as a function of its solubility may be achieved by investigating the elemental distribution between the extract and residue fractions. The first application to real samples strongly suggests a further deepening of the environmental significance of the obtained fractions. Particularly, the possibility of obtaining some simplified information by the sole analysis of the extract fraction, by an already well-established approach for soils and sediments, should be carefully evaluated as it would permit a very fast and inexpensive screening of environmental data. On the other hand, a deeper investigation of results on metals distribution obtained by fully applying of the proposed procedure can provide the comprehension of phenomena influencing the distribution and could consequently give rise to new tracers for the ageing and emission sources identification of airborne particulate matter.

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