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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 A: Experimental design and optimisation

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Abstract

The optimisation of a micro-analytical two-step sequential leaching procedure for the determination of non-volatile ions (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, NH_4^+ and Ca^{2+}) and of 17 elements (Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Se, V, Zn, Sb, Si and Ti) in two fractions—extract and residue—on the same sample of air particulate matter is described. The two-step method was tested on the SRM NIST 1648 for equivalence with two reference methods, the EMEP procedure for ions extraction and the EN 12341 standard for the elemental determination of the PM_{10} and is suitable for application to small sample amounts (less than 1 mg of particulate matter is needed), i.e. those collected by daily low volume filter-sampling. Performance times of the procedure were optimised to meet the target of routine application for large scale monitoring samples. A single ultrasonic-assisted extraction of air particulate matter is performed in 0.01 M acetate buffer at pH 4.5, followed by IC ions analysis and ICP-OES elemental analysis of the extract and by ICP-OES elemental analysis of the mineralized residue after dissolution by microwave-assisted digestion with a HNO_3/H_2O_2 mixture. Using a pH buffered extracting solvent was preferred to water or diluted acid solutions to improve the reproducibility of metals extraction with respect to existing leaching methods; the influence of pH, nature and concentration of the buffer solution and extraction time on analytes concentration in the extract is discussed. Values of ions extraction and elements recoveries resulted fairly equivalent with those obtained by the reference methods. The study was also extended to some non-certified elements (Mg, S, Sb, Si and Ti) for their environmental significance. Elements recoveries were obtained as sum of the extract and residue fractions and were comparable with those obtained by direct dissolution. Standard deviations were within 10% for almost all detected ions and elements.

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1. Introduction

The chemical characterization of airborne particulate matter (PM) has a key role in evaluating the effects on human health, ecosystems and materials [1,2], as well as in the improvement of understanding the chemical processes of PM in the atmosphere for research and modelling scopes [3,4–6]. Many different chemical species can be used as markers of PM sources and precursors [7,8]; non-volatile ions are representative of secondary air pollution events, whereas trace metals have high chemical stability related to peculiarly different relative composition in particulates from different emission sources [9,10].

Bio-geochemical distribution and toxicity of an element are dictated by its particular species or forms present in a given real matrix [11] and, in this sense, the total elemental determination is insufficient today to assess the availability and reactivity of the element to different real matrixes. Chemical fractionation approaches were recently reviewed [12] and allow to get "operational" information on the chemical forms of a wide range of elements, bound to the experimental conditions applied and to the environmental and/or biological behaviour of the PM investigated, that is related to the emitting source [13].

Sequential leaching is commonly used to evaluate the mobility of trace metals, combined with multi-elemental analysis of each fraction and frequently with the determination of non-volatile ions [14,15]. Most different methods are available, based on sequences of four [16,17] or three steps [18–20]. However, these are scarcely applicable to low-volume airborne PM

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samples commonly collected on daily basis under legislative obligations [21–23], being time-consuming and requiring PM mass amounts well higher than 1–2 mg or less obtained by low-volume daily sampling.

Some methods have also been developed properly for low-volume [24] and/or specifically for 24 h low-volume sampled filters [25,26], based on two sequential extractions and followed, or not, by dissolution of the residue. To our knowledge, however, only few examples are found in recent literature of two step-only schemes in which a single extraction is performed, followed by digestion of the residue and combined with multielemental and ions determination [27,28]. In these latter methods extraction of PM is performed by water or diluted acid solutions.

However, an aqueous solution in equilibrium with sampled filters shows a pH variability usually included in the 3–5 pH range [29]. These pH values should not substantially affect the solubility of ions whose acid–base equilibria are negligible (like Na^+, K^+, Cl^- and NO_3^-) and of ions which are present in the same prevalent species in the whole range (like SO_4^{2-}). On the other hand, the extract fraction of most of the considered metals, which are subjected to hydrolysis equilibria, is expected to vary as a function of pH, which in its turn changes due to release of acids and neutralizing agents during the dissolution process. Using a pH buffered solution as extracting solvent has been thus preferred, to ensure reproducibility in the metals distribution between extract and residue fractions.

In this view a two-step micro-analytical leaching procedure has been developed, in which the extraction is performed in a pH buffer solution, that is targeted at analysis of small amounts of PM on Teflon filters by low-volume sampling and is suitable for routine application to large-scale air monitoring on daily basis.

Equivalence with the EMEP reference procedure was assessed to the purpose of analyzing the non-volatile ions content in the same extract solution of trace metals. To this aim, results are discussed of the study of different pH buffer solutions. These were investigated for suitability as extracting solvents with respect to water extraction, also to ensure the robustness of the procedure in reproducibility by maintaining at the same time the equivalence with reference methods.

2. Experimental

2.1. Reagents

The following reagents have been used: deionised H_2O (MilliQ), HNO_3 (65%, RPE, Carlo Erba, Rome, Italy), H_2O_2 (30%, Suprapur, Merck), HF (40%, Suprapur, Merck.), glacial CH_3COOH (Carlo Erba), CH_3COOK (p.a. Sigma), ion chromatography (IC) and inductively coupled plasma (ICP) standards (Merck).

The accuracy of the sequential leaching procedure was evaluated by analysing the reference material NIST 1648 (National Standard Institute of Technology, USA), whose employment is suggested by European Committee for Standardization (CEN) for elemental analysis of PM. This material is a natural atmospheric coarse matter non-filter-collected in an urban location and is certified for the total content of 15 elements.

2.2. Analytical procedure

Weighted amounts ranging from 1 to 2 mg of NIST 1648 were placed in polyethylene tubes, added of 5 mL of extracting solution and exposed to ultrasonic irradiation (28/34 KHz, 80/180 W) for variable times (3–20 min). Homogeneity of ultrasonic (US) irradiation was assured by a home made rotating device.

The extract was then filtered on cellulose nitrate filter, (Millipore, 0.45 μm pore size, previously washed with 20 mL of extracting solution) and 5 mL of extracting solution were passed through the filtering device to obtain a quantitative recovery and added, obtaining 10 mL of final extract solution. A 2 mL portion was withdrawn and used for ions chromatographic analysis and the remaining volume was used for ICP elemental analysis of the extract fraction. After extraction each filter was transferred to a PTFE vessel and 4 mL of 65% HNO_3 and 2 mL of 30% H_2O_2 were added to each vessel [31]. The vessels were placed in microwave (MW) oven (Milestone Ethos Touch Control equipped with HPR 1000/6S rotor) and digested by a two-step temperature-time program. In the first step the temperature was linearly increased to 180 °C in 8 min with a maximum power of the rotating magnetron of 650 W. In the second step the temperature was kept at 180 °C for 15 min. After digestion and cooling down, each obtained solution was filtered on Millipore nitrate cellulose (NC) filters previously treated with HNO_3 10% (w/w) for 24 h and filled up with ultrapure H_2O to10 mL, obtaining the mineralized residue fraction.

Polyethylene tubes used for sample storage and the leaching step were pre-cleaned by two rinses of 10 mL deionised water. The PTFE digestion vessels were cleaned, before and after using, with a two-step time program for temperature in the same microwave oven used for samples digestion. Each vessel was added of 4 mL 65% HNO_3 and 2 mL 40% HF. In the first step the temperature was linearly increased to 180 °C in 4 min with the rotating magnetron at a maximum power of 1000 W. In the second step the temperature was kept at 180 °C for 9 min at a maximum power of 650 W. After cooling the vessels were rinsed with deionized water and, where not directly used, filled with HNO_3 10% (w/w). This cleaning procedure is necessary to assure the removal of silicates and aluminium and chromium oxides which can likely form.

2.3. Ion analysis

A DX-100 Dionex and a Metrohm 761 Compact ion chromatographs were used to determine respectively non-volatile cations (Na^+, Ca^{++}, Mg^{++} and NH_4^+) and anions (NO_3^-, SO_4^{2-} and Cl^-) in the extract fraction using 2 mL of the extract solution. The anions were determined using a Metrohm Supp 5 column equipped with anionic suppressor. The eluent was 9.6 mM $NaCO_3$/3.0 mM $NaHCO_3$ (isocratic) at a flow rate of 0.65 mL/min. The cations were determined using a Dionex ION PAC CS12A-4 mm column equipped with a pre-column ION PAC CG12A-4 mm and a suppressor CRSR-ULTRA 4 mm. The eluent was 20 mM methanesulphonic acid (CH_4O_3S) (isocratic) at a flow rate of 1.0 mL/min.

2.4. Elemental analysis

The concentrations of seventeen elements (Al, As, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, S, Sb, Se, Si, Ti, V and Zn) were determined in both extract and mineralized residue fractions obtained from each sample using a simultaneous ICP–OES (Varian ICP/VISTA MPX) equipped with an ultrasonic nebulizer (U 5000 AT^+, Cetac Technologies Inc.). Standard solutions for calibration were matrix—matched by preparation in 0.01 M CH_3COOH/CH_3COOK solution (pH 4.5) or HNO_3 10% (w/w). Analytical blanks were performed on filters from the same batch, on polyethylene tubes and on PTFE vessels. The blank was a reagent + vessel + laboratory-glass and for all metals were lower than 20% of measured values. A subtraction of blanks (calculated as the mean value of six replicated measurements) was in any case applied to all results.

The ICP-OES operating parameters, which were properly optimised to meet the appropriate detection limits, are given in Table 1 together with the reading and control wavelenghts and the LOQ at a 5% R.S.D. Certified values of each metal related to the application of the procedure to 1 mg of NIST are also reported for comparison.

Table 1
Analytical conditions for elemental analysis

ICP–OES instrumental parameters

Incident plasma power (RF) 1.30 KW
Plasma gas flow 16.5 $L\,min^{-1}$
Auxiliary gas flow 1.50 $L\,min^{-1}$
Nebulizer pressure 230 KPa
Replicate read time 30 s
Instrument stabilization delay 45 s
Sample uptake delay 15 s
Pump rate 1.2 mL/min
Rinse time 10 s
Replicates 3

Detection parameters and LOQs (R.S.D. ≤5%)

Element	Reading wavelength (nm)	Check wavelength (nm)	LOQ (μg/L)	Certified values on NIST 1648[a] (μg/L)
Al	396.152	394.401	2	3400
As	188.980	193.696	2	12
Cd	214.439	226.502	0.1	7
Cr	267.716	284.984	0.1	40
Cu	327.395	324.754	0.2	60
Fe	238.204	259.940	0.02	4000
Mg	279.553	280.270	0.01	–
Mn	257.610	260.568	0.05	80
Ni	231.604	227.021	0.6	8
Pb	220.353	405.781	1	650
S	180.669	181.972	20	–
Sb	206.834	217.582	4	–
Se	196.026	–	2	2.5
Si	251.611	288.158	5	–
Ti	336.122	337.280	0.1	–
V	311.837	309.310	0.5	13
Zn	206.200	213.857	0.2	480

[a] Values related to 1 mg of NIST 1648 in a volume of 10 mL.

Table 2
Choice of the extracting solution—experimental conditions

	Initial pH	Concentration range (mol/L)	US time (min)
Phosphate buffer	2, 3, 4.5, 7	0.001–0.1	20
Acetate buffer	4.5	0.001–0.1	3–20

2.5. Choise of extracting solutions and interferences

Extracting solutions to be investigated were chosen on the basis of interferences on IC and ICP analyses, which may arise from the salt used as pH buffer because of overlapping peacks in chromatograms and of impurities. In Table 2 the investigated solutions, together with the experimental conditions applied are reported. The use of citrate buffer was not further considered, after some preliminary tests, because of its prohibitive chromatographic interferences on anions detection. Both acetate and phosphate peaks resulted well separated in the anion chromatogram by the chosen conditions (tr(acetate) = 5.1 min and tr(phosphate) = 9.3 min). Nevertheless, at buffer concentrations higher than 0.01 M broad and tailed peaks were observed with an increase of uncertainty, respectively in the determination of Cl^- (tr(chloride) = 7.5 min) in the acetate solution and of SO_4^{2-} (tr(sulphate) = 11.2 min) in the phosphate solution.

As for cations analysis sodium, potassium and lithium ions have been investigated for interferences when used as counter ions of the salt used as pH buffer. Of these, only Li^+ in particulate matter is not to be determined under the EMEP reference method and could be thus used as counter ion instead of other cations to be analysed. However, when Li^+ has been used for this purpose a significant worsening in the resolution of Na^+ and NH_4^+ peaks was observed, which couldn't be avoided by arrangement of the IC analysis protocol. Further studies are in progress therefore to improve this problem. Among the other cations investigated potassium has been preferred to sodium in the phosphate and acetate salts, both for chromatographic reasons (as at high Na^+ concentrations its peak gives a partial overlapping with NH_4^+) and because of the environmental significance of Na^+ determination in marine aerosols [32].

Buffers impurities were determined by IC and ICP OES analysis of blanks of the extracting solution and resulted lower than 10% of values commonly expected for real samples using both buffers and in any examined conditions

3. Results and discussion

3.1. Choice of the extracting solution

First, a study on the extracting solution to be used to obtain the leacheable fraction of metals and ions was carried out. The choice of the optimal leaching solution was made basing on the following requirements: (a) pH buffering capacity of the solution and (b) equivalence with the EMEP reference ions extraction procedure [22].

The effects due to the presence of hydrolysis and complexation equilibria have not been taken into account as discriminating

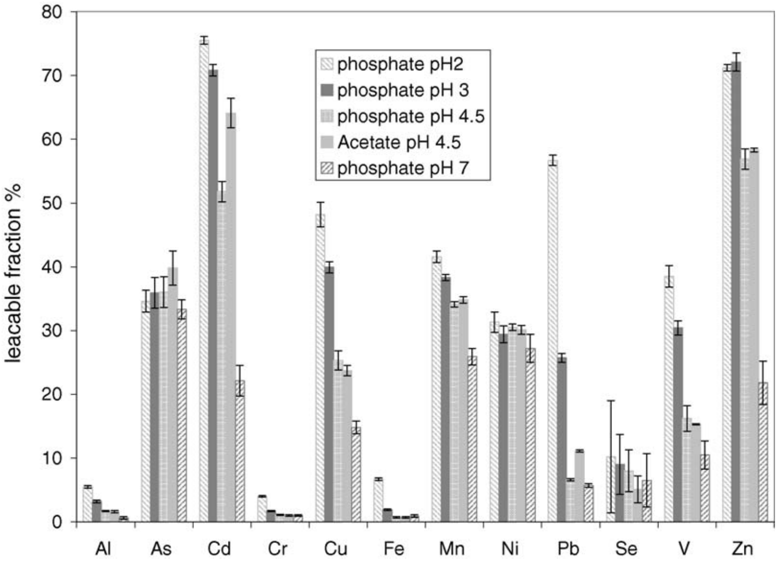

Fig. 1. Comparison of the extract fraction of elements, calculated as percentages of certified values, obtained on SRM NIST 1648 with different pH buffered solutions. Error bars were calculated from six replicates and incude interdiurnal variability.

factor on the optimisation of procedure, due to the acknowledged consideration that sequential extraction procedures lead to a purely operational definition of the leached fractions [13] and information provided on the different "mobilities" of metals are strictly dependent on the operative conditions by which the extraction has been carried out.

Moreover, whatever extracting solution is chosen with respect to its ability in resembling the environment-spontaneous physico-chemical conditions of a given matrix which act on the leaching of a given PM, it could not be perfectly reliable at any rate.

Therefore, in our opinion, the achievement of an acceptable level of reproducibility is a key requirement in the development of new sequential extraction methods.

3.1.1. pH and buffering capacity of the extracting solution

The extracting solution must ensure that pH at equilibrium keeps constant with no regard to the chemical composition and the amount of collected samples. Although high buffer concentrations provide *a priori* a good buffering capacity, the choice of as low as possible buffer concentration was necessary in order to minimize operative blanks, avoid an inconvenient broadening of chromatographic peaks and reduce saline deposits on ICP torch. The buffering capacity of each solution was thus assessed by measuring pH before and after the extraction of NIST 1648 (ca. 5 mg). Acetate or phosphate concentrations $\leq$0.005 M showed an inadequate buffering capacity at any pH, while a concentration of 0.01 M was adequate at pHs 2, 3 and 7 for phosphate and 4.5 for acetate. To the aim of evaluating the effect of complexation equilibria on extraction percentages a phosphate solution adjusted at pH 4.5 was also considered, despite its low buffering capacity, after previous achievement of equilibrium.

In Fig. 1 the percentages of NIST 1648 extraction at different pH conditions are reported for each certified metal, which were calculated with respect to the certified values. With the exception of Se, whose low reproducibility is due to its concentration in the extract below the ICP LOQ (see Table 1), the percentage R.S.D. are for most metals lower than 10% and seem not to depend on the buffer pH and nature, at least for homogeneous samples like those obtained by a SRM.

As expected, Fig. 1 shows that pH of the leaching solution strongly affects the extraction percentages of most metals and a general decrease of solubility is observed with the increase of the pH value, according to the increased weight of hydrolysis equilibria. This result confirms that a pH buffered extracting solution is needed to avoid that metals partitioning between the extract and residue fractions could be dependent on the species which determine the intrinsic acidity of particulate. On the other hand, the extraction percentages at pH 4.5 obtained by both acetate or phosphate extraction are comparable within the experimental error, indicating the low contribution of complexation equilibria on metals partitioning. The only exceptions are lead and cadmium, whose extract fraction is significatively higher in the presence of acetate. Complexation with acetate is particularly strong, indeed, for these two metal ions [33], so that complexation equilibria may compete efficiently with hydrolysis and, for lead, with $PbSO_4$ solubility equilibria. This hypothesis is also confirmed by the dependence of the metals extraction percentages on the acetate concentration (Fig. 2). Extraction percentages showed a general increase with buffer concentration for almost all the considered metals, whereas significantly large increases of percentage extracted lead and to a lesser extent cadmium, were observed, ranging from $(6.0 \pm 0.4)\%$ to $(46.5 \pm 0.8)\%$ for lead and from $(53.7 \pm 0.6)\%$ to $(68.1 \pm 0.7)\%$ for cadmium.

3.1.2. Equivalence with the reference ions extraction procedure

To test the reliability of the leaching method under development in determining the ions content in the same extract of metals, that is one of the primary aims of this work, equivalence of results of ions extraction by leaching in buffer solution

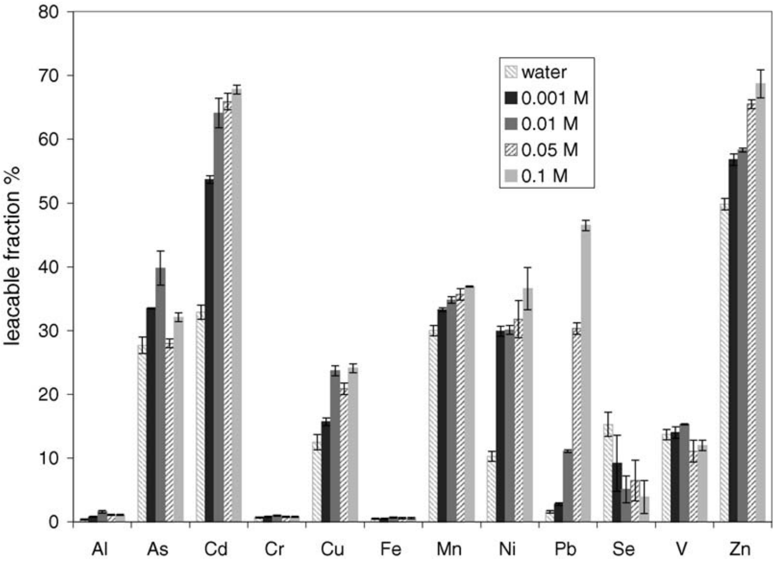

Fig. 2. Influence of acetate buffer (pH 4.5) concentrations on the extract fraction of elements, calculated as percentages of NIST 1648 certified values. Error bars were calculated from six replicates and incude interdiurnal variability.

was assessed with respect to the water extraction indicated by the EMEP reference ions extraction procedure from airborne aerosols [22].

The obtained results (Fig. 3) confirm a low dependence of concentrations of the extracted ions on the composition of the leaching solution. Indeed, with the exception of magnesium and calcium ions, whose concentrations tend to increase at low pH values, and of sulphate ion at pH 2, equivalence of results is within the standard deviations in all the examined conditions. Dependence on pH of Mg^{2+} and Ca^{2+} extract amounts arises possibly from the different degree of protonation of the carbonates and from the solubility equilibria of oxides. However, this indicates, also for these ions, that using a pH buffered extracting solution is appropriate to avoid variability of the extract fraction with the particulate acidity. Sulphate ion is extracted in larger amounts at pH 2, probably due to the occurring of protonation equilibrium at this pH, which favours the extraction of low-soluble salts.

On the basis of the above discussed results, the 0.01 M acetate buffer at pH was chosen as extracting solution, also taking into account that pH values around 4.5 are environment-spontaneous [29].

Before starting the validation of the sequential procedure for the recovery of metals, the extraction efficiency was also investigated with respect to its dependence on the time of treatment by ultrasonic bath and a time of 15 min was found adequate to perform a complete extraction of both ions and metals.

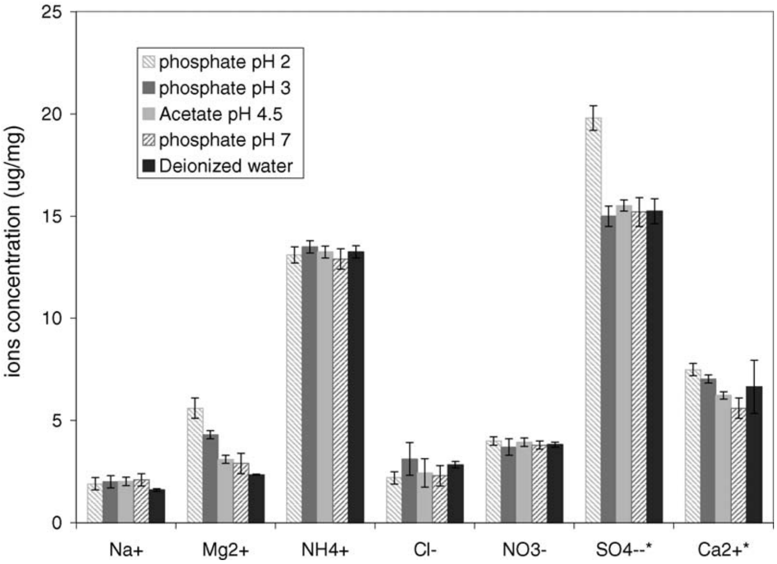

Fig. 3. Comparison of ionic concentrations extractable by different pH buffered solutions with repect to deionised water. Values related to SO_4^- and Ca^{2+} were divided by 10. Error bars were calculated from six replicates and incude interdiurnal variability.

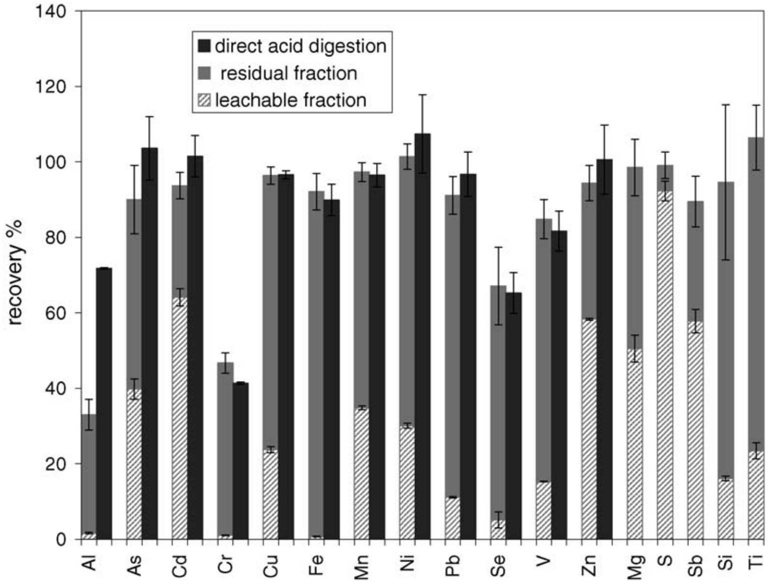

Fig. 4. Comparison between the recovery percentages obtained from NIST 1648 by either direct acid digestion or the two-step sequential procedure. Recovery percentages were calculated with respect to the certified values. For non-certified elements recoveries were calculated with respect to values obtained by direct acid digestion. Error bars were calculated from six replicates and incude interdiurnal variability.

3.2. Recovery of metals

The accuracy of the analytical procedure in the determination of metals has been tested by evaluating the recovery obtained as the sum of metal content in the extract and in the mineralized residue fractions with respect to the metal total content certified on the SRM NIST 1648.

A microwave assisted direct acid digestion procedure was previously carefully optimised by authors [31], that is based on a $HNO_3 + H_2O_2$ digestion mixture and whose dissolution efficiency had been found to provide total recovery percentages close to 100%, except for Al and Cr, on the NIST 1648. The choice of not including in this digestion mixture HF for decomposition of silicates was mainly due to reasons of higher blank contribution [31,34] and of lower data reproducibility, which mainly arise from the sample treatment used for the un-reacted HF removal prior to the ICP-OES analysis [31]. The direct digestion with HNO_3/H_2O_2 mixture was then considered as reference procedure to evaluate the performance of the new procedure, also in agreement to the CEN standard [30]. Thereby, the study was also extended to some non-certified elements (Mg, S, Sb, Si and Ti), whose recoveries from application of the two-step procedure were calculated with respect to their content experimentally obtained by direct acid dissolution of NIST 1648.

Determinations of elemental sulphur, which should be found in air PM samples almost completely as sulphate, and magnesium were indeed included in the study with the purpose of having an internal check of consistency of the ions determination, while Ti and Sb have been investigated for their environmental significance.

Si and Al were included too, even though their dissolution efficiency in HNO_3/H_2O_2 mixtures is expected to be very low, because of their primary role in the assessment of natural contribution to the air-suspended particulate matter and, therefore, in the perspective of having more complete information on their solubility equilibria available from the future field-test applications of the two-step method.

As shown in Fig. 4, with the exception of Al, results obtained applying the two-step method are largely comparable with those from direct dissolution, for both certified and non-certified elements, confirming that the method ensures the accuracy requirements. Also, concentrations of extract Mg and S resulting from ICP-OES elemental analysis (respectively 3.0 ± 0.1 and 51.5 ± 1.3 μg/mg) are consistent with those determined by IC.

Reproducibility is also assured, as the percentage R.S.D. (calculated on six replicates) resulting from the application of the sequential procedure show the same magnitude order than those related to the direct acid digestion, and are well below 10% for almost all detected elements. Particularly, for the extract fraction very low percentage R.S.D. values have been obtained, ranging between 0.1% of Fe and 3.6% of Mg and most being around 1.5%.

For the mineralized residue fraction R.S.D.% values in the range 1.3–6.5%, respectively for Mn and Ti has been obtained, evenly distributed and comparable with those resulted from the direct dissolution of the sample, which showed values between 0.2% of Al and 10.4% of Ni. Silicon showed, as expected, a high R.S.D.% in the mineralized residue (20.6%; of the same magnitude order of the 19.2% one associated to the direct acid dissolution), but extracted Si content is fairly reproducible, with a R.S.D.% = 3.7%. The fact that total percentage recovery of Al obtained with the tested method is far lower than the one obtained by direct dissolution can be addressed to the possible formation of insoluble Al oxides during the US treatment.

Crustal elements, whose total recoveries are well below 100%, could be determined more accurately by non-distructive techniques, as XRF or PIXE. However, it's in our opinion that data showing a good reproducibility could maintain an environmental interest in comparative field studies despite their poor accuracy.

Moreover, preliminary results indicate that the metals distribution between the two fractions is in some cases affected by the storage conditions and by the conditioning step of NIST 1648, requiring thus to be carefully evaluated in the next future.

4. Conclusions

The optimised two-step extracting procedure allows to perform on the same sample of air particulate matter the elemental analysis and the extracted ions determination by a single extraction step in a pH buffered solution and is targeted at analysis of small amounts of PM on Teflon filters by low-volume sampling. The analytical performances of the tested procedure are comparable, for accuracy, reproducibility and time of analysis, to those obtained by applying separately to airborne PM the standard methods for ions extraction and elemental analysis. Combining the chemical characterization of inorganic ions and elements on small PM amounts, only in a single extraction step and in the residue mineralized, allowed to minimize samples manipulation and laboratory operations, thus reducing costs, time for analysis and further sources of error.

The total metal content is obtained by the two fractions, which are reasonably associated, as yet largely recognized for soils and sediments, to different environmental mobilities and health impacts.

Since in this work the SRM NIST 1648 was used, which is a coarse urban particulate and non filter-collected, the procedure needs to be further validated on real samples of filter-collected PM_{10} and $PM_{2.5}$ and tested for suitability to routine application to large-scale air monitoring on daily basis.

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