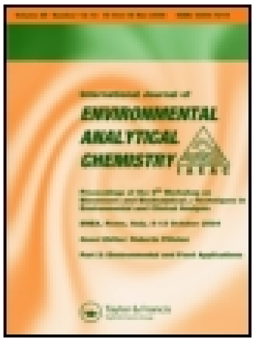

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ARTICLE

Comparative study of bulk and partial digestion methods for airborne PM_{10}-bound elements in a high mineral dust urban site in Constantine, Algeria

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ABSTRACT

When high mineral loads in atmospheric particulate matter (PM) are present, particular attention should be paid to the selection of appropriate acidic digestion protocols for wet chemical analysis. We report on a comparative study of elemental recovery yields from five different pre-analytical acid digestion procedures for mineral-rich urban background PM_{10} samples collected in the city of Constantine (Northeastern Algeria). Five reference materials (NIST 1633b, UPM 1648, NAT-7, SO-2 and SO-4) were also digested according to the same protocols. The selected acidic digestion/extraction procedures are widely used for PM chemical analysis and comprise P1 (HNO_3/HF/HCl), P2 (HCl/HNO_3), P3 (HCl/H_2O_2/HNO_3), P4 (HNO_3/HF/$HClO_4$) and P5 (HNO_3/H_2O_2); the latter assisted with microwave digestion. Elemental recovery yields were compared for major and trace elements typically determined in PM for source apportionment analysis and the results evidenced large differences. For most elements, the bulk extraction procedures (requiring the use of HF) allowed a full elemental recovery, particularly for elements that are associated with aluminium silicate species and oxides that are resistant to mild acid attack. In contrast, in the extraction protocols without HF low recovery yields were obtained for elements such as Al, Ti, Zr, Sc and other aluminium silicate-related elements in PM_{10} samples with high mineral dust load. We highlight that the European standard digestion method EN-14902:2005 should be applied specifically for the metals for which this method was developed, but caution should be taken when the analysis of other elements in PM is required, especially in urban areas where road and vehicle wear dust is likely to be a major component of ambient PM. When using wet chemistry analysis for PM source apportionment studies, we strongly recommend HF bulk dissolution of samples to ensure the reliability of the geochemical information when coupled with an appropriate analytical tool.

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1. Introduction

The chemical analysis of atmospheric particulate matter (PM) sampled in ambient air at very low concentrations is a challenge, not least because the low weights of the samples increase the risk of loss and contamination. Furthermore, the diverse modes of occurrence of major and trace constituents, and the widely varying nature of PM components in different settings need to be taken into account when using pre-analytical extraction or digestion procedures for subsequent wet chemistry. In recent years, analysts have recognised increasingly that systematic errors can be introduced during the sampling and sample preparation steps [1].

Different digestion/extraction methods for elemental analysis of atmospheric PM can be used, and their extraction efficiency depends on several factors, the most relevant of these being sample compositional nature, the type of acidic mixture used, the type of energy applied (conventional and/or microwave heating) and the temperature and duration of the digestion [2]. In the scientific literature, these various digestion/extraction procedures for major and trace elements in PM (and related materials such as sediments, soil, deposited dust samples, wastes and biological samples) are reported commonly without specifying whether the type of extraction chosen achieves total dissolution of specific metals or whether it is selective for specific elemental fractions. Some such studies are based on a single-step digestion/extraction and use different mixtures of reagents such as HNO_3 + HCl (*aqua regia*), HNO_3 alone, HNO_3 + H_2O_2, HNO_3 + HF + H_2O_2 + H_3PO_4, HNO_3 + HCl + HF, HNO_3 + HF [2–6]. Other procedures implement sequential extraction protocols designed to partition different elements based on both their mode of occurrence in the samples and the different solutions applied [7–9]. Different heating systems can be also used, such as sand bath, hot plate, pressure digestion vessels and aluminium blocks [4,10], or the assistance of microwave during the heating system (reducing the amount of reagents and time required) [11]. Another key parameter concerns the requirements of the analytical protocol with regards to the compositional patterns of the final solutions arising from the acidic digestion. Thus, the presence of HF in the final solution may cause instrumental problems or a high content of Cl might yield relevant spectroscopic interferences in ICP-MS determinations.

A bulk digestion method for most inorganic environmental samples should include the use of HF, which, despite its problematic use in laboratory, remains the only reagent capable of digesting silicates, aluminium silicates and some resistant oxides (such as TiO_2) [11–13]. If the samples to be analysed contain relevant fractions of these components, as is the case with urban PM_{10} or those from desert areas such as PM from North African cities, the use of non-destructive analytical tools, such as XRF (X-Ray Fluorescence), INAA (Instrumental Neutron Activation Analysis), PIXE (Particle Induced X-Ray Emission) or digestion procedures involving HF, is required for a bulk chemical characterisation. Siliceous mineral dust is not only common in PM from arid or semi-arid environments, but also characterises many urban areas where abrasion of road pavement by traffic, the use of studded tyres in winter and agricultural and construction emissions produce a significant loading of ‘crustal’ PM_{10}. Digestion of such materials with acid mixtures without using HF runs the risk of poor extraction performances for some elements. Thus whereas in many studies other methods such as *aqua regia* have been found to be similarly effective to HF digestion for some specific elements [10], this milder extraction procedure is less useful for analysing others. As an example, Peña-Icart et al. [14] compared two partial digestion methods and found that neither of the two methods can replace the bulk HF digestion for Cu, Pb and Ni. Similarly, Mathews et al. [15] compared two partial extraction methods with two bulk digestion procedures using soil samples and found significant differences for Cd, Cu, Mg, Ni, Pb and Zn. In contrast, Celo et al. [4] used two standard materials (SRM 2783 and 1648) for comparing the extraction with HNO_3 (40%) and the bulk HF digestion for Ni, V, Zn, Co, Cd, Cr, Mn, Pb, As and Se and concluded that the extraction procedure provides a viable alternative to bulk HF digestion for almost all of their studied elements. A more detailed study was carried out by Sastre et al. [10], using 10 reference materials and 25 real samples with different environmental matrices for comparison of three acidic digestion/extraction methods: bulk HF digestion, extraction with *aqua regia* and HNO_3. The study confirmed that the use of *aqua regia* for the digestion of samples rich in organic matter was the best choice because this procedure was less expensive and faster than the bulk digestion. Such alternative extraction/digestion procedures are developed to provide a quicker and easier dissolution of the sample with a lower consumption of reagents. However, these procedures must provide comparable results with a sufficiently high reproducibility for the elements in question. They should at the very least dissolve the organic matter and the easily digestible inorganic compounds in the sample [16].

The European Commission has defined concentration limits for specified toxic elements in their air quality directives: As, Cd, Ni (Directive 2004/107/EC) and Pb (Directive 1999/30/EC) [17]. The European Committee for Standardization went on to develop a standard method for the measurement of these toxic metals and metalloids (Pb, Cd, As and Ni: EN-14902:2005) [18], recommending the use of HNO_3 and H_2O_2 as reagents and microwave as a source of energy. This standard procedure was the choice of several studies [17,19,20] based on the repeatability of results and the limits of detection of most elements which were found to be better than the ones obtained when HF was added. However, it has been recognised that this approach may lead to incomplete recovery for some elements such as Al, Si and Cr [19].

This present study aims at improving our understanding of the potential problem posed by elements resistant to dissolution by non-HF procedures by comparing the effectiveness of five widely used digestion/extraction procedures in PM_{10} samples containing relatively high loads of mineral dust in order to evaluate when partial extraction/digestion procedures can be accepted as alternative procedures to bulk digestion using HF. For this purpose, reference materials (with certified values and/or reference to elements) of different matrices and concentrations of elements are used in addition to a set of actual mineral-rich urban PM_{10} samples. Although the effectiveness of an extraction procedure can only be quantified using standard samples having certified or reference values for the elements of interest, these do not necessarily reproduce the digestion efficiency of a given procedure for filter-collected PM_{10} samples or the concentration ranges of a specific study [4,21]. In this case we do not have certified reference values but we can compare the relative extractions yields of the different acidic digestions for the elements studied.

2. Experimental

2.1. *Samples*

Five reference mineral-rich materials were selected:

- NIST 1633b: A coal fly ash with a dominantly aluminium silicate composition.
- SRM 1648: An urban PM sample with an unknown load of mineral matter.

- NAT-7: A deposited urban dust sample with an unknown mineral load. This is not a certified reference material, but concentration data are available from a large IAEA (International Atomic Energy Agency) round-robin inter-laboratory inter-comparison exercise.
- SO-2: A soil certified reference material with high mineral load.
- SO-4: Another soil certified reference material with high mineral load.

In addition to these standard materials, 10 PM_{10} samples were collected from 15 January 2015 to 12 March 2015 at an urban/suburban background site in the Faculty of Earth Sciences 'Zouaghi Slimane' at the University of Mentouri Brothers in Constantine (Northeastern Algeria) using a high-volumes ampler (Tisch Environmental, TE 6070). The ten 24 h samples were collected on quartz microfiber filters (20 cm × 25 cm). After each sampling interval, the collection media were humidity and temperature stabilised for 24 h in a desiccator before weighing with a precision less than ±0.01 mg using a Shimadzu balance (model AUW120D). The initial weights were determined after a similar period of desiccation of the blank filter.

2.2. *Acidic digestion procedures*

We chose two bulk and three partial extraction procedures; one of the latter being assisted by microwave. Extraction procedures were applied using different acid mixtures as described elsewhere [4,14,22,23]. These procedures have been slightly modified to be adapted to our laboratory conditions. Thus, the procedures were carried out in PFA (PerFluorAlkoxy) vessels and reactors in all cases, with the exception of the P5 procedure, which used PFM (PerFluorinatedMonomer), even when HF (which may yield a significant release of glassware-bound elements in the solutions) was not used in order to harmonise operating conditions and avoid altering the composition of the digestion extracts. Moreover, the digestion time was adapted to the containers used. To complete each extraction procedure, two circular pieces of 25 mm diameter discs were cut from the 10 PM_{10} filters. The five extraction procedures labelled as P1, P2, P3, P4 and P5 are described below. For all procedures and for each material used, two replicates were prepared. Filter blanks were treated exactly as the samples in each digestion protocol and the blanks were subtracted of the filter samples to obtain elemental ambient concentrations.

2.2.1. *First procedure (P1)*

This procedure is based on the method proposed by Kuvarega and Taru [22]. Filters were placed in PFA vessels containing 2.5 mL of HNO_3 (20%) and left in contact for 4 h and then 0.75 mL of HNO_3 were transferred to the vessels, which were then heated on a hot plate until evaporation at 240°C. The vessels were left to cool down at room temperature and then 0.5 mL HNO_3 was added. The solutions were heated again to partial drying, and 0.5 mL of HF was added to reach bulk dissolution and then driven to dryness at 240° C. The vessels were left to cool down and then 2.5 mL of milli-Q water was added. The solutions were transferred into 25 mL vials and adjusted to the desired volume with a solution containing 1% HCl and 0.7% HNO_3. Finally, the solutions were filtered to remove potential insoluble residues.

2.2.2. *Second procedure (P2)*

This method is based on the method proposed by Peña-Icart et al. [14]. The samples were introduced into PFA vessels, 10 mL of a solution (3:1) (37% HCl and HNO_3 70%) were added and the vessels were left for 24 h. They were then heated on a hot plate (240°C) for 15 min. The solution was filtered and the volume was completed to 25 mL with 3% HNO_3. This is the ISO 1146.3 digestion, one of the most widely used partial digestion methods for sediments.

2.2.3. *Third procedure (P3)*

This procedure is based on the method proposed by Awan et al. [23]. The extraction of filters was carried out with the following reagents: HCl (37%), H_2O_2 (35%) and HNO_3 (65%). Samples were introduced in PFA vessels and 30 mL HCl and 5 mL H_2O_2 were added. The vessels were then heated for 1 h on a hot plate at 240°C. After cooling, the solutions were filtered and 20 mL HCl (18.5%) was added to the remaining residue for 15 min to complete the extraction. The solution was then filtered and added to the first filtrate. The final solution was concentrated on a hot plate until a small volume was obtained and transferred to a volumetric flask of 25 mL. The full volume was completed with 1.5% HNO_3 solution.

2.2.4. *Fourth procedure (P4)*

This procedure is based on the method proposed by Querol et al. [12]. The samples were digested in a solution (1 mL HNO_3 and 2 mL HF) in closed PFA reactors at 90°C for at least 8 h. After cooling, the containers were opened and 1 mL of $HClO_4$ was added. The mixture was then driven to complete dryness by placing the open PFA bombs on a hot plate at 240°C. The remaining dry residue was dissolved by adding HNO_3 and distilled water (milli-Q), obtaining a 5% HNO_3 solution. Finally, the latter was brought to 25 mL with milli-Q water.

2.2.5. *Fifth procedure (P5)*

This process complies with the European standard digestion method EN-14902:2005. The digestion process takes place in a microwave oven with 8 mL HNO_3 at 70% + 2 mL of H_2O_2 at 30%. The microwave oven was programmed to reach 220°C in 25 min, then was kept to that temperature during 25 more minutes and finally was cooled down during 15 min. It was finally transferred and diluted with milli-Q water to a final volume of 25 mL.

2.3. *Analytical techniques*

All the obtained solutions from PM_{10}, reference materials and blank filters were then analysed by ICP-AES (IRIS Solutions Advantage Thermo TJA) for Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Sr, Ti, V and Zn and by ICP-MS (X Series II Thermo) for Li, Be, Sc, Cr, Co, Ni, Cu, Ga, Ge, As, Se, Rb, Y, Zr, Nb, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Sm, Gd, Dy, Hf, Tl, Pb, Bi, Th, U and H-REES (heavy rare earth elements) which include Pr, Sm, Gd and Dy and L-REES (light rare earth elements) which include La, Ce and Nd [24]

3. Results and discussion

3.1. *Recovery yields of major and trace elements in the reference materials*

The most common approach to measure the effectiveness of sample digestion procedures is the estimation of the percentage of elemental recovery/extraction of elements from the standard materials with similar physical and chemical features to that of the actual samples from a specific study [11]. To interpret the differences observed between the five extraction procedures, it is essential to recall the compositional features of the five acidic digestions and the theoretical dissolution targets of the mixtures. Both P1 and P4 procedures use HF and are devised to allow the determination of bulk elemental concentrations in the samples [6]. The *aqua regia* (P2) is frequently used for the extraction of metals in sample matrices, but does not dissolve specific residual minerals such as aluminium silicates or resistant oxides [6,12]. The addition of H_2O_2 and $HClO_4$ in P3 and P4 allows extraction of the oxidisable phases (i.e. sulphides and organic matter) [7]. HNO_3 is usually added to H_2O_2 (P5) for the dissolution of organic matrices and specific minerals such as sulphate, carbonate and phosphate minerals, among others [25]. Microwave acidic digestion is widely used for its advantages in terms of rapidity and simplicity [26]. Procedure (P5) follows the EU reference protocol used for the determination of Pb, Cd, As and Ni found in $PM_{10,}$ and it has been used in a number of recent studies for PM chemical characterisation studies [17,19,20,26]. Chemically, if the reagents mixture is unable to break down the sample completely, no device would achieve its complete dissolution [25]. Since the matrices used as reference materials were of different types, a wide variation of elemental extraction yields is to be expected among the acidic protocols applied.

The elemental concentrations obtained from analysis of the different reference materials using the five acidic digestion procedures are compared below. The list of certified/reference/'for information' elements for each standard material is presented in Table 1.

The following 36 elements were analysed (by ICP-AES and ICP-MS) and have certified, reference or 'for information' values for the reference materials selected: Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Sr, Ti, V, Zn, Sc, Cr, Co, Ni, Cu, As, Se, Rb, Cd, Sb, Cs, La, Ce, Nd, Sm, Gd, Dy, Hf, Tl, Pb, Th and U, as well as 10 elements Li, Be, Ga, Ge, Y, Zr, Nb, Sn, Pr and Bi that have no reference values for any of the five certified materials but we evaluated the extraction yields for them and the five protocols in a relative way. Figure 1 shows the recovery yields for all these elements and protocols.

3.1.1. *Reference material NIST 1633b*

This is mainly an aluminium silicate material because it is made of high Si–Al coal fly ash. This reference supplies concentration data for 21 certified elements and 15 additional, non-certified (for information) elements (Table 1). The elemental recoveries attained by procedures P1 and P4 with regards to this reference material are very satisfactory, with extraction yields of the major elements ranging from 78% to 111% for P1 and from 97% to 117% for P4 (in most cases falling into the uncertainty given for them in the certifications). Zn for P4 reached 127% probably due to sample contamination.

Table 1. Certified and non-certified (*for reference only) concentrations of major and trace elements in the five reference materials.

Element	Unit	NIST-1633b	NIST-1648a	NAT-7	SO-2	SO-4
Al	%	15.05	3.43	3.57*	8.07	5.46
Ba	mg kg^{-1}	709	–	–	966	–
Ca	%	1.51	5.84	2.38*	1.96	1.11
Fe	%	7.78	3.92	5.44*	5.56	2.37
K	%	1.95	1.06	0.99*	2.45	1.73
Mg	%	0.482	0.813	–	0.54	0.56
Mn	mg kg^{-1}	131	790	658*	720	600
Na	%	0.201	0.424	–	1.9	1
P	mg kg^{-1}	2300*	–	–	3000	900
S	%	0.208	5.51	–	–	–
Sr	mg kg^{-1}	1041	215	–	340	170
Ti	%	0.791	0.402	0.25*	0.86	0.34
V	mg kg^{-1}	295	127	99.9*	64	90
Zn	mg kg^{-1}	210*	4800	1887*	124	94
Sc	mg kg^{-1}	41*	–	–	–	–
Cr	mg kg^{-1}	198	402	424*	16	61
Co	mg kg^{-1}	50*	17.9	14.9*	9	11
Ni	%	120	81.1	250*	8	26
Cu	mg kg^{-1}	112	610	1616*	7	22
As	mg kg^{-1}	136	115.5	23.43*	–	–
Se	mg kg^{-1}	10	28.4*	–	–	–
Rb	mg kg^{-1}	140*	51	–	78	–
Cd	mg kg^{-1}	0.78	73.7	–	–	–
Sb	mg kg^{-1}	6*	45.4	192*	–	–
Cs	mg kg^{-1}	11*	3.4*	–	–	–
La	mg kg^{-1}	94*	39*	–	–	–
Ce	mg kg^{-1}	190*	54.6	–	–	–
Nd	mg kg^{-1}	85*	–	–	–	–
Sm	mg kg^{-1}	20*	4.3*	–	–	–
Gd	mg kg^{-1}	13*	–	–	–	–
Dy	mg kg^{-1}	17*	–	–	–	–
Hf	mg kg^{-1}	6*	–	–	–	–
Tl	mg kg^{-1}	5.9*	–	–	–	–
Pb	mg kg^{-1}	68	6550	639*	21	16
Th	mg kg^{-1}	25.7	–	–	–	–
U	mg kg^{-1}	8	–	–	–	–

P1 and P4 recovery yields are also good for trace elements, with only a few values exceeding 120%, also probably due to contamination or spectrometric interferences (Cd, for P1 and Se, Cd, Gd, for P4). The lowest recovery yields obtained for P1 and P4 are 57–74% for Cs.

As expected, P2, P3 and P5 (not including HF in the acidic mixtures) did not achieve complete dissolution of the silicate-bound elements [12,27,28] and this produced low elemental extraction yields for the majority of the analysed major and trace elements. As examples, Al and Ti were extracted with recoveries of 16–23% and 19–29%, respectively, whereas high recovery yields are reached with P1 and P4 (78% and 99% for Al and 93% and 98% for Ti). A number of elements usually associated with aluminium silicate minerals, such as Sc, Cr, Rb, Cs and L-REEs, Hf and Th were also barely recovered by P2, P3 and P5 (with recoveries <40%), whereas near bulk concentrations were obtained for P1 and P4 digestions.

Another group of elements that are usually present in high proportion in the aluminium silicate fraction includes Ba, Mg, Sr, V, Be, Co, Ni, Cu, Y, H-REEs, Tl, Pb and U. These elements were recovered by P2, P3 and P5 with only 30–60%. Better results

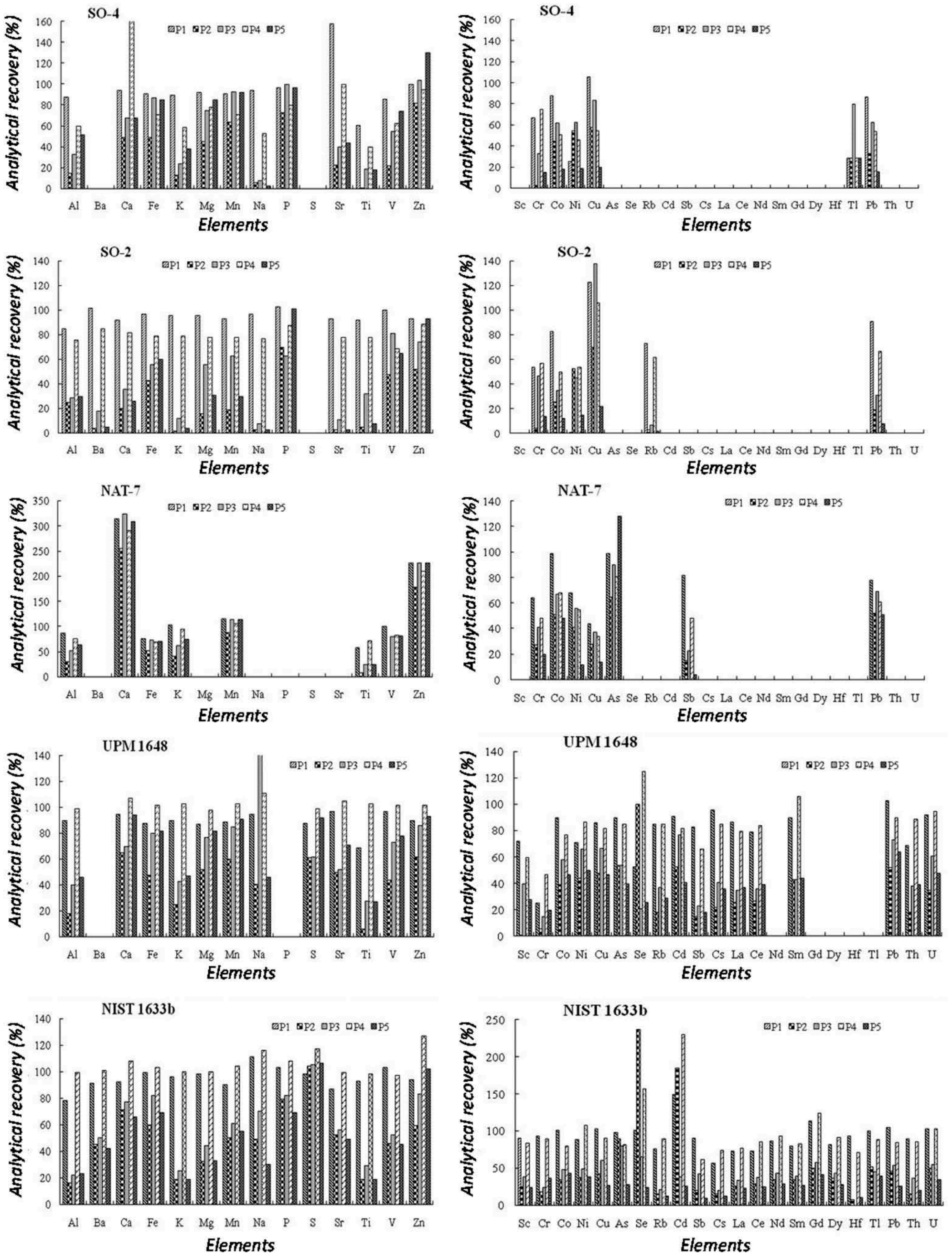

Figure 1. Recovery yields (%) for major and trace elements in the reference materials according to the five extraction procedures P1, P2, P3, P4 and P5.

were achieved for Ca, Fe, Na, P, Se and Cd recoveries when applying P2, P3 and P5 (>60%), but were still clearly lower than those reached with P1 and P4. Recovery yields for S ranged from 98% to 117% for all procedures. All methods were also relatively efficient for the extraction of As (80–98%), except for P5 (28%).

Although P2, P3 and P5 achieved comparable elemental extraction efficiencies, procedure P5 was much less effective than P2 and P3 for As, Se, Cd, HREEs, Tl and Pb; and P3 was more efficient for almost all elements than P2.

3.1.2. *Reference material UPM 1648*

This reference material is made of urban PM and the occurrence of aluminium silicate species and resistant oxides are to be expected from the likely presence of road dust, construction dust and other mineral dust sources. UPM 1648 certification supplies reference values for 22 elements and non-certified data for 4 elements (Table 1). As expected, procedures P1 and P4 proved to be the most efficient, P4 being slightly more efficient for 65% of the elements.

The recovery yields for Cr for P1 and P4 reached only 25% and 47%, respectively. For the rest of the studied elements, the rates ranged from 69% to 103% for P1 and from 60% to 111% for P4. For P2, P3 and P5, recoveries were lower than 47% for K, Ti, Cr, Sc, Rb, Sb, Cs, most REEs and Th; again elements occurring in aluminium silicate minerals.

Method P3 was more efficient than method P2 for 80% of the elements with differences ranging from 1% to 39%. The addition of H_2O_2 allowed increasing recoveries for Fe (80%), Mg (77%), Mn (85%), Zn (86%), V (73%), Cd (77%) and Pb (73%). P5 and P3 elemental recoveries were comparable in 72% of the elements evaluated, with differences lower than or equal to 20%.

3.1.3. *Reference material NAT-7*

This urban dust is not a certified material, but it supplies reference concentrations for 15 elements from large laboratory round-robin exercises (Table 1). It is an urban dust sample and again a relatively high mass contribution of mineral matter might be expected.

Again, P1 and P4 recovery yields for NAT-7 were markedly higher compared to P2, P3 and P5 for the elements studied. Overestimated values were observed for Ca and Zn for the five extraction procedures indicating probably the inaccuracy of reference values. Relatively low recoveries (lower than 70%) were observed for Ti, Cr, Ni and Cu for P1 and for Fe, Cr, Co, Ni, Cu, Sb and Pb for P4, but both procedures achieved a predictably high recovery for the remaining elements. Ti, Cr and Sb were barely recovered by partial digestion procedures P2, P3 and P5 with recoveries less than 41%. Recoveries of Al, Ni and Cu by the same methods were also low (8–63%), whereas those of Mn and V were high (exceeding 80%).

P3 procedure was more efficient than P2 in recovering almost all of the elements with reference concentrations for this non-certified material, with differences ranging from 9% to 73%. The recovery yields of Fe, Mn, V, Cu, Cd and Tl ranged from 72% to 113%. When comparing P3 and P5, the first reached 12–13% higher recovery yields for Al and K, but lower (by 19–44%) yields for Cr, Co, Cu, Sb and Ni.

3.1.4. *Reference material SO-2*

This is a soil sample with a high mineral content and contains certified concentration values for 19 elements (Table 1). Very high recoveries were obtained by the bulk extraction procedure P1, and slightly lower by P4, for almost all elements. For most elements recoveries reached 73–123% for P1 and from 62–106% for P4. Out of these, Cr recovery yield reached 54% for P1, while those of Cr, Co and Ni attained 50–57% for P4. Again as expected, partial digestion procedures P2, P3 and P5 proved inefficient recoveries, lower than 36%, for Al, Ca, K, Ti, Ba, Na, Sr, Co, Se and Pb. Slightly higher recovery yields were obtained for Cr, Fe, Mg and Mn, while V and Zn were highly recovered with rates ranging from 48% to 93%.

Procedure P2 was the least effective for the elemental recoveries as very low ones were obtained for Ba (4%), Na (3%), Sr (3%), Cr (4%), K (2%), Ti (5%) and Rb (3%), while the remaining certified elements were extracted with rates between 16% and 70%. P3 was more efficient than P2 (with differences of 4–68% and an average of 21%). Procedure P5 can be classified as intermediate between P2 and P3 in terms of elemental recovery efficiency as H_2O_2 accelerates the oxidation of organic material present in the sample so that procedure P5 achieved better rates than P2. The dissolution of organic fraction in P5 outweighed the dissolution of inorganic fraction by HCl present in P2. Procedure P5 was less efficient than P3 for 78% of the elements.

3.1.5. *Reference material SO-4*

This reference material is also a soil sample with a high mineral content and supply certified concentration values for 17 elements (Table 1).

Once again the highest extraction performances were obtained for P1 and P4, with the exception of Tl (with recovery yields for both procedures reaching only 29%) and Ni (with 26% and 46%, respectively). Na, Co, Cu, Pb and Ti were slightly recovered by P4 with recovery yields ranging from 40% to 55%. P1 was more efficient than P4 for all elements with the exception of Ca, Cr and Ni.

P5 was clearly more efficient than P2 for the majority of elements with an average difference of 26% ranging from 1% to 52%. Methods P2, P3 and P5 showed low extraction efficiencies for K, Na, Ti, Cr and Tl with recoveries lower than 38%. On the other hand, Ca, Fe, Mg, Mn, P and Zn were extracted in a relatively high proportion by these three partial digestion procedures, with recoveries ranging from 45% to 100%. Thus, higher extraction yields were obtained for the SO-4 reference material when using non-bearing HF acidic extractions in comparison with SO-2. Both samples are soil samples but do not necessarily have identical compositional features in terms of mineralogy and chemistry.

The addition of H_2O_2 in the P3 procedure improved the recoveries of elements in the SO-4 reference material. These ranged from 8% to 104%. The addition of H_2O_2 in P3 allowed an increase of the dissolution capacity of *aqua regia* and speeds up the oxidation of organic matter present in the sample [26].

3.1.6. *General findings for the reference materials and elements*

As expected, the differences on the extraction yields reached using various digestion methods varied widely with the elements and the physicochemical patterns of the reference materials. Figure 2 shows the average recovery yields of major and trace elements in the reference materials (NIST 1633b, UPM 1648 NAT-7, SO-2 and SO-4) according to the different extraction procedures.

If we assume that uncertainties in analysis results do not exceed 20%, we may not take into consideration overestimated values from 100% to 120%, neither

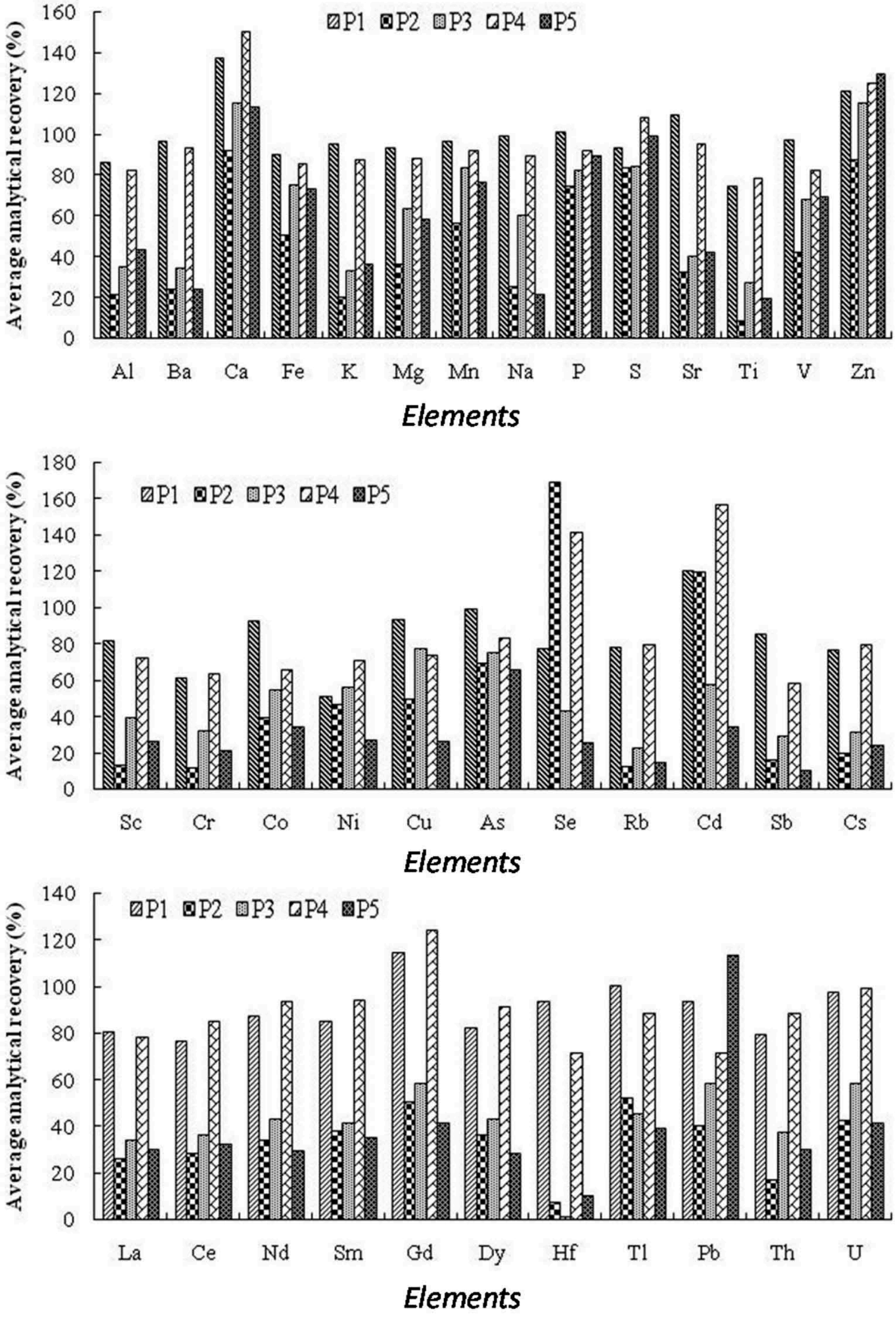

Figure 2. Mean recovery yields for major and trace elements contained in the reference materials (average values for NIST 1633b, UPM 1648, NAT-7, SO-2 and SO-4) according to the five digestion procedures P1, P2, P3, P4 and P5.

underestimation from 80% to 100%. Both P1 and P4 bulk digestion procedures were found to be very effective for elemental recoveries, with average values ranging from 82% to 109% for Al, Ba, Fe, K, Mg, Mn, Na, P, S, Sr, As, HREEs, Pb, Th and U. Overestimated results, probably due to contamination, were obtained for Se, Cd and Gd and Zn for P4 (NIST 1633b, where the Zn concentrations were only given for reference and not certified), Ca and Zn for P1 and P4 (NAT-7, where reference concentrations were not certified but averaged values for round robin exercises) and Ca for P4 (SO-4). Both HF-based digestion protocols were close enough to the bulk concentrations reported for the analysed standard materials NIST 1633b, UPM1648 and NAT-7. However, procedure P1 was more efficient than P4 for standard materials SO-2 and SO-4 for almost all elements.

As expected, partial digestion procedures P2, P3 and P5 did not achieve the bulk contents of most of the elements. Low recovery yields (lower than 50%) in all reference materials were obtained for Al, Ba, K, Sr, Ti, Sc, Cr, Rb, Sb, Cs, REEs, Hf and Th. Recovery yields exceeded 49% for at least 75% of the results for Ca, Fe and Mn. The highest extraction yields with important discrepancies were determined for V (44–81%), Co (12–67%), Ni (12–66%), Cu (14–70%), As (28–89%), and Gd (41–58%), probably due to the different modes of occurrence of these elements in the reference materials. Thus, as an example, V can occur in easily soluble V-oxides, or V(III) might substitute Al (III) in aluminium silicates, the latter only soluble when HF is used in the acid attack. Also, relatively good results exceeding 50% were observed for P, S and Zn.

3.2. *Recovery yields of major and trace elements in PM_{10} samples*

Figure 3 reports data on daily ambient air PM_{10} mass concentrations for the samples collected from 15 January 2015 to 13 March 2015. These varied from 14 to 99 µg m^{-3} with an average value of 44 µg m^{-3}. Averaged concentrations were high, being double the recommended World Health Organization Air Quality Guideline for annual averaged PM_{10} concentration, with the wide range in daily values reflecting variations in the contributions of natural (mostly desert dust) and anthropogenic emission (road traffic, industry, domestic and residential, construction works, among others). These variations in PM source contributions are likely to affect results from the different extraction protocols when applied to samples obtained during different days. Thus, days with the lowest PM_{10} concentrations will be characterised by a low mineral load, with high relative contributions of sulphate and nitrate species and organic matter, both easily dissolved using HNO_3, H_2O_2 and HCl mixtures. However, days with high loads of African dust or high road traffic derived PM_{10} will be characterised by a PM_{10} composition rich in aluminium silicate loads that will require HF for effective elemental recoveries during the sample digestions. Thus, even though all samples may be PM_{10} collected at the same location, elemental recovery yields for a given non-HF-bearing extraction mixture will vary as a function of the daily PM loading.

Figure 4 shows the average concentrations of major and trace elements in the 10 urban PM_{10} samples using the five digestion procedures. Table 2 shows in addition a comparison between the ratios of recovery yields (%) for the different extraction methods and the selected elements, taking as a reference the mean concentration

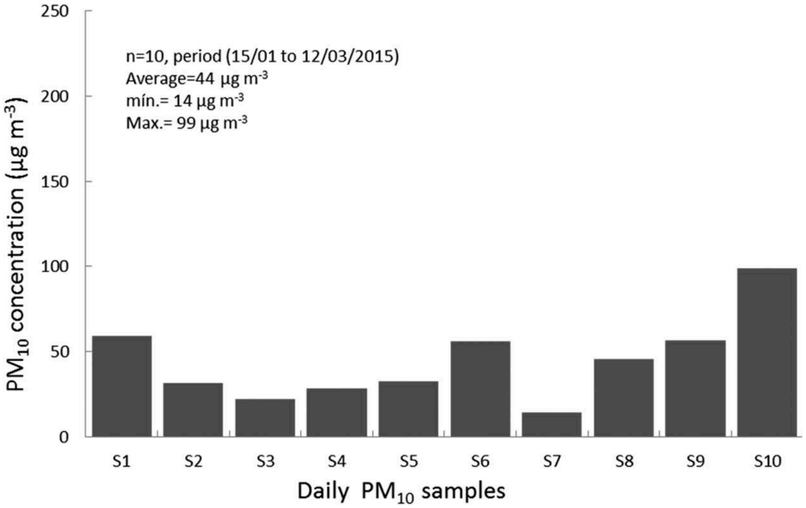

Figure 3. Daily atmospheric PM_{10} concentrations.

obtained for P4. Elements have been grouped taking into account the extraction efficiency in the following descending order: P4, P1, P3, P5 and P2.

Concentrations of Be, Sc, Ge, Cs, Tl and Bi were below the detection limits for the majority of PM_{10} samples. It should be noted also that ambient concentrations measured for Co, Se, Cd, Sn, Sb, Sm, Gd, Dy and U in PM_{10} were less than 2 ng m^{-3}, making difficult comparison of the digestion yields in many cases. For elements present in PM_{10} in higher contents however, which is the case for the major elements and some trace elements such as Al, Ba, Ca, Sr, Ni, Ti, Cu, Mn, Zn and Pb, the two bulk digestion procedures (P1 and P4) led to similar concentrations, which, as expected, were markedly higher than those obtained by partial extraction procedures P2, P3 and P5.

The lowest recovery yields for P1, P2, P3 and P5 compared to those of P4 (less than 30%) were obtained for Zr and Nb (usually occurring, along with Hf, Th and REEs, in the mineral zircon, a zirconium silicate that is highly resistant to acid attack). The need for using HF for dissolving these species and the higher temperature and pressure reached during P4 versus P1 probably accounted for this difference.

P1/P4 ratios ranged from 30% to 60% for Cr and Hf and from 60% to 120% for Al, Ba, Ca, Fe, K, Mg, Mn, Na, P, S, Sr, Ti, V, Zn, Li, Cu, Ga, Rb, REEs, Pb and Th. The P4 protocol was more efficient than P1 for all elements with the exception of V, Co, Cu, Ga, As, Se, Rb, Y, Cd, Sb, REEs, Pb, Th and U; and more efficient than P2 for almost all elements with the exception of Se, HREEs and Th.

The ratios P2/P4 were lower than 30% for Al, Ti, Cr, Zr, Sn and Hf, from 30% to 60% for K, Mg, Sr, Li, Ga, Rb, Y and LREEs, and exceeded 60% for Ba, Ca, Fe, Mn, Na, P, S, V, Zn, Cr, Co, Ni, Cu, Ga, As, Se, Cd, Sn, Sb, HREEs, Pb, Th and U.

The ratios P3/P4 were lower than 30% for Al, Ti, Cr, Zr, Sn and Hf, from 30% to 60% for Mg, P, Sr, Zn, Li, Ni, Cu, Ga, As, Rb, Y, Nb and LREEs, and exceeded 60% for Ba, Ca, Fe, K, Mn, Na, S, Ti, Co, Se, Cd, Sb, HREEs, Pb, Th and U.

The ratios between the average concentrations determined for P5/P4 were lower than 30% for P, Ti, Zr, Nb and Hf, from 30% to 60% for Al, K, Mn, Sr, V, Cr, Ga, As, Y, Cd

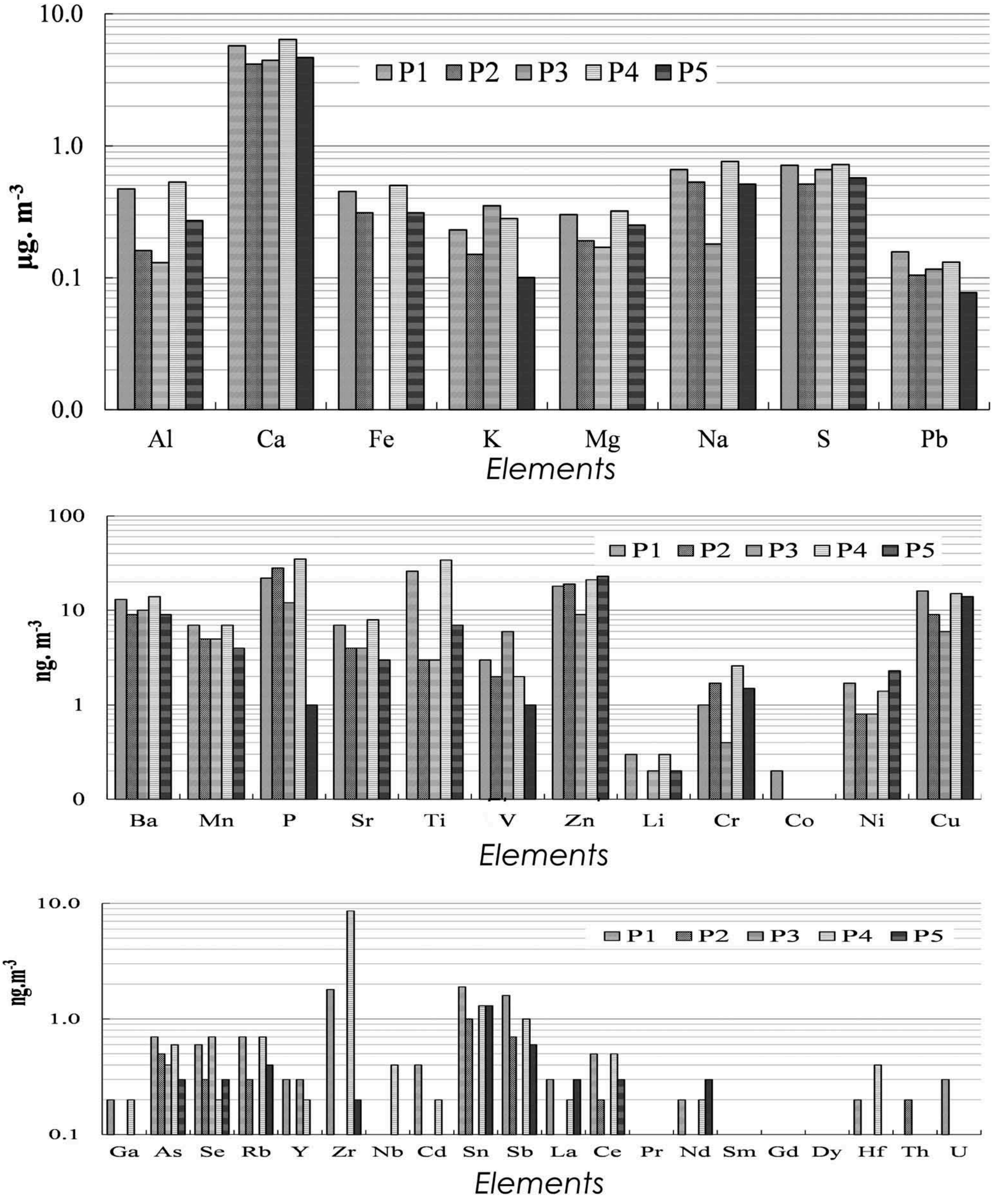

Figure 4. Mean concentrations of major and trace elements in PM_{10} samples as determined by the five different extraction procedures P1, P2, P3, P4 and P5.

and Pb, and exceeded 60% for Ba, Ca, Fe, Mg, Mn, Na, S, Zn, Li, Co, Ni, Cu, Se, Rb, Sn, Sb, REEs, Th and U.

The mean concentration of V and As obtained by P3 was significantly higher than those obtained with other extraction procedures. This may be due to a spectral interference of Cl–Ar for these elements during ICP-MS analysis. Cl was present in the digestion solution where acid evaporation might not have been completed during P3 digestion. The partial extraction procedures P2, P3 and P5 proved to be

Table 2. Elemental recovery yields for PM_{10} samples.

	P1/P4	P2/P4	P3/P4	P5/P4	P2/P1	P3/P1	P5/P1	P2/P3	P5/P3	P2/P5
					%					
Al	89	30	24	51	33	27	57	124	213	58
Ca	90	65	69	73	73	78	81	94	105	89
Fe	88	62	69	63	70	78	71	90	91	99
K	84	54	62	36	64	74	43	87	58	150
Mg	93	58	55	78	62	59	83	105	141	74
Na	87	69	86	67	79	99	78	80	78	102
S	98	70	68	79	72	69	81	104	117	89
Ba	94	65	71	63	69	76	67	91	89	103
Mn	90	66	72	48	74	79	53	93	67	138
P	64	79	34	3	124	54	4	230	8	2790
Sr	94	55	54	43	58	57	45	102	80	128
Ti	78	8	9	22	10	12	28	90	238	38
V	113	75	243	42	67	214	37	31	17	180
Zn	85	89	44	107	105	52	125	201	241	83
Li	97	39	59	68	40	61	70	66	114	58
Cr	40	66	16	57	167	40	144	412	355	116
Co	151	63	75	68	42	50	45	85	91	94
Ni	126	62	55	164	49	44	130	111	298	37
Cu	107	60	41	94	56	38	88	149	232	64
Ga	115	59	36	57	51	31	50	164	159	103
As	124	89	703	49	72	569	39	13	7	184
Se	300	144	269	132	48	90	44	53	49	109
Rb	108	39	59	63	36	55	58	65	105	62
Y	126	50	53	48	40	42	38	94	90	105
Zr	20	2	1	2	8	6	11	144	185	78
Nb	29	29	49	26	100	169	87	59	52	115
Cd	206	82	61	54	40	29	26	135	89	152
Sn	140	76	29	96	54	21	68	259	325	79
Sb	160	71	68	65	45	42	40	106	9	111
La	118	36	53	138	30	44	117	68	262	26
Ce	106	39	58	68	37	55	64	67	117	58
Pr	99	87	87	87	88	88	88	100	100	100
Nd	98	44	53	103	45	54	105	83	195	43
Sm	137	134	134	134	98	98	98	100	100	100
Gd	171	163	163	163	96	96	96	100	100	100
Dy	191	163	163	163	85	85	85	100	100	100
Hf	57	28	28	27	48	48	47	100	97	103
Pb	119	79	88	59	66	74	49	90	66	135
Th	103	213	103	103	208	100	100	208	100	208
U	260	91	91	91	35	35	35	100	100	100

Percentage recovery values for P1, P2, P3 and P5 relative to those obtained for P4.

equivalent among them and this is in contradiction with the results observed in the case of reference materials where addition of H_2O_2 improved the recovery efficiency of *aqua regia*. Nevertheless, differences were observed regarding P, Zn, Cu, Cr and Sn which were extracted in higher proportions by P2 while Pb was better extracted by P3.

In the case of PM_{10} samples, the differences between partial digestion procedures varied in one way or another, but for nearly half of the elements, the concentrations were similar. This can be explained by the different matrix composition of real PM_{10} samples compared with standard materials. This is the reason why comparative studies between different extraction procedures used for the digestion of environmental samples are not always consistent. Figure 5 shows the impact of the selected digestion procedure on evaluating time trends of selected elements in PM_{10}, and in a number of cases conclusions might be very different.

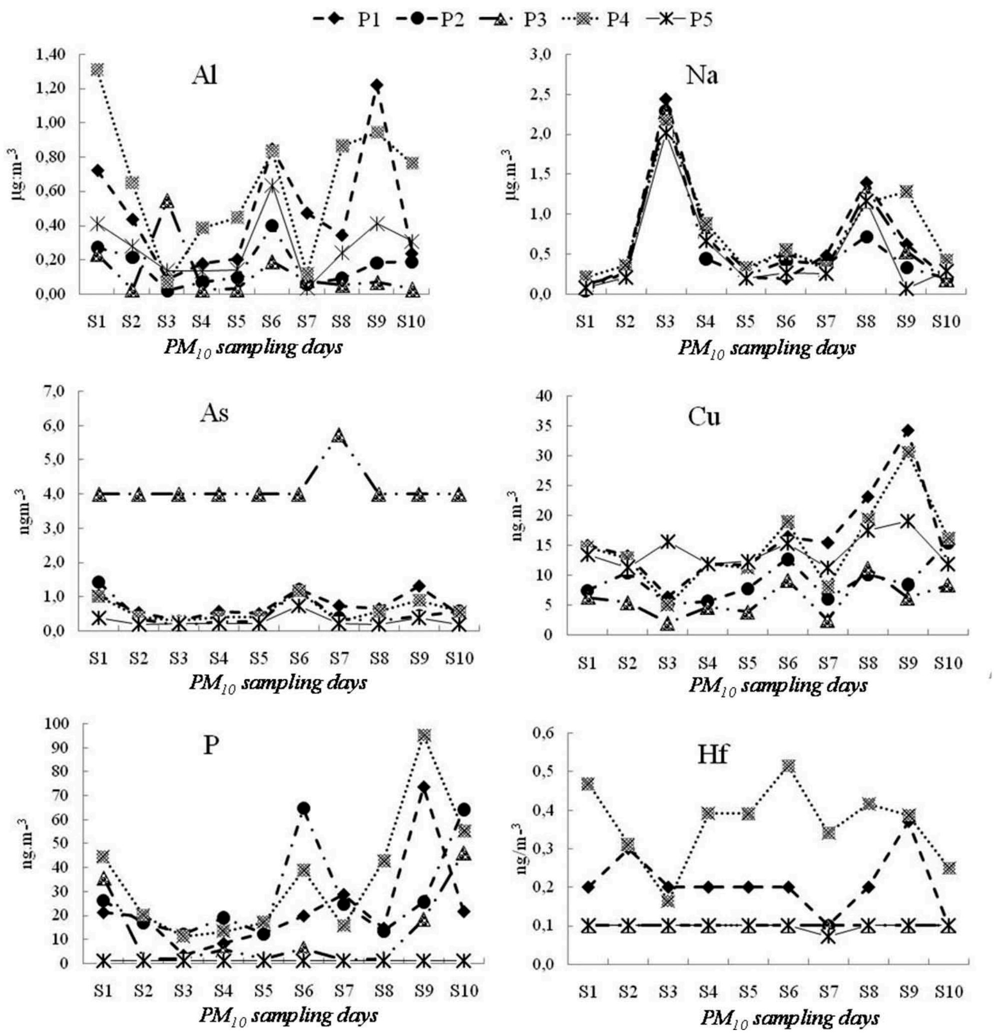

Figure 5. Variation of atmospheric concentrations of selected elements in the 10 actual high dust urban background PM_{10} samples according to the five digestion procedures P1, P2, P3, P4 and P5.

On the basis of the results of this study, we can confirm that the use of HF ensures approaching total extraction of the major and trace elements contained in the different types of high mineral dust urban PM_{10} samples. Some of the studied elements may be well recovered (with elemental recoveries for references materials and ratios compared to procedure P4 for real samples higher than 75%) with the non-HF-bearing acidic mixtures P2, P3 and P5 (Table 3). If an element contained in a given sample has been highly recovered by a partial digestion procedure in the absence of HF, it means that the proportion bound to the resistant mineral fraction (resistant aluminium silicate or resistant oxides such as anatase or rutile, both TiO_2) is not high. Table 3 confirms the similarity of the two partial digestion procedures P3 and P5 with regards to 50% of elements in terms of efficiency in the case of reference materials. As mentioned before, P5 conforms to the European standard EN-14902:2005 method for the determination of

Table 3. Partial extraction procedures alternative to bulk HF digestion depending on the element considered and the sample type.

Element	NIST 1633b (fly ash)	UPM1648 (urban particulate matter)	NAT-7 (urban dust)	SO-2 (soil)	SO-4 (soil)	PM_{10} samples
Ba		P5				
Ca	P3	P5				
Fe	P3	P3, P5			P3, P5	
Mg		P3, P5			P3, P5	P5
Mn		P3, P5	P2, P3, P5		P3, P5	
Na						P3
P	P2, P3			P5	P3, P5	P2
S	P2, P3, P5	P5				P5
V		P5	P3, P5	P3		P2
Zn	P3, P5	P3, P5		P5	P2, P3, P5	P2, P5
Co						P3
Cu					P3	P5
As	P2, P3					P2
Pr						P2, P3, P5
Nd						P5
Cd		P3				P2
Tl			P5		P3	
Th						P3, P5
Pb						P2, P3
U						P2, P3, P5

Cd, Pb, As and Ni in the PM_{10}. Certainly, this method has proven to be very efficient for extracting these four elements for samples that were used for the certification of this procedure. Our results demonstrate that this is not the case when applied to the extraction of a number of certain other elements, and this should be taken into account when devising studies on PM chemistry. Furthermore, it is also important to completely evaporate Cl in the dissolutions arising from acidic mixtures containing HCl and $HClO_4$ since spectral interferences for relevant elements such as As and Se can cause significant problems.

4. Conclusions

According to our results, the elemental extraction yields of five acidic digestion procedures applied to reference materials and actual PM_{10} samples might vary from one sample to another, from one matrix to another and from one element to another. In general, bulk digestion methods (P1 and P4) were very effective for the elemental recovery of all of the studied elements. Extraction with *aqua regia* (P2) proved to be less effective in the majority of cases. The addition of H_2O_2 in the P3 and P5 procedures led to more or less satisfactory results for certain elements contained in the standard materials in comparison with the results obtained by P2. The partial extraction methods P2, P3 and P5 applied to real PM_{10} samples proved also to be much less efficient than P1 and P4 procedures, but none of them stood out from the others. In fact, the effectiveness of a partial extraction procedure with regards to the reference materials could not always be extrapolated to real environmental samples if compositional and mineralogical patterns are not very close or if these might change from day to day (as is the case with PM_{10}). In any case, our results confirm that the effectiveness of partial digestion procedures for defined samples and elements cannot be generalised to all cases, even when different PM_{10} samples from the same site are evaluated.

This study demonstrates the major influence of the chosen acid digestion procedure on the recovery yields of major and trace elements in samples containing significant amounts of mineral matter using samples of urban PM_{10} from a North African city. The results show that the methods not using HF might achieve high extraction yields for a limited number of elements and in specific sample matrixes. We also demonstrate that even for PM10 samples from the same location fluctuation of the mineral load in urban aerosols might give rise to different extraction yields if HF is not used in the dissolution processes. To avoid such problems, for wet chemistry PM-based source apportionment studies (where a large number of elements are required) we strongly suggest the use of HF-bearing and high temperature and pressure acidic digestion methods (such as P4) favouring complete recovery in most of the cases. It should be noted that no reagents mixture or microwave assistance can replace the presence of HF, which, despite its problematic use in laboratories, remains the only reagent capable of releasing major and trace elements bonded to silica, aluminium silicates and resistant oxides such as rutile and anatase (TiO_2). Furthermore, independently of the digestion system used, Cl has to be completely evaporated before obtaining the final dissolutions for ICP-MS analysis to avoid important spectroscopic interferences. Finally, the data reveal that the European standard EN 14902:2005 extraction procedure for metals in PM_{10} should not be applied to elements other than those for which it was specifically designed. For high dust loads, the elemental recovery of specific elements using non-HF methods might be far from their true bulk contents in ambient PM_{10}.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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