Journal of Earth Sciences and Geotechnical Engineering, vol. 7, no.1, 2017, 137-149
ISSN: 1792-9040 (print), 1792-9660 (online)
Scienpress Ltd, 2017

Comparative Study of Three Digestion Methods for Airborne PM10-bound Metallic Elements in an Urban Site

Amina Kemmouche[1], Hocine Ali-Khodja[1], Xavier Querol[2] and Fayrouz Bencharif-Madani[1]

Abstract

A comparative study of three different aerosol extraction processing techniques was carried out on ten quartz fiber PM10 sampling filters and a standard material (P1633b Fly Ash). Simultaneous sampling of PM10 was conducted at an urban background site in the town of Constantine. Three different mixtures of reagents were chosen in order to achieve the extraction procedure: mix 1 (HF / $HClO_4$ / HNO_3), mix 2 (HCl / HNO_3), mix 3 (HCl / H_2O_2 / HNO_3). A standard material (P1633b) was used to quantify and compare the extraction efficiencies of the three techniques. The solutions obtained after dust mineralization were analyzed by two analytical techniques. Pb, Cu, Co and Ni were analyzed by ICP-MS, while Zn and Mn were determined by ICP-AES. The first digestion technique proved to be the most efficient for all samples. The differences in extraction efficiencies between the three techniques varied from one sample to another according to the element analyzed.

Keywords: PM10, partial extraction, metallic elements, digestion methods

1 Introduction

Particulates are compounds with a health issue and their study is important because they are small enough to penetrate the respiratory system (Al Masri *et al.*, 2005). These pollutants can be primary when they are directly emitted to the atmosphere or secondary when they result from the transformation of gaseous pollutants. The emission sources of aerosols are diverse. They may be natural such as soil erosion, the bursting of waves bubbles allowing the formation of sea spray, volcanic activity, etc. (Azimi, 2004).

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[1] Laboratoire Pollution et Traitement des Eaux (LPTE), Département de Chimie, Faculté des Sciences Exactes, Université des Frères Mentouri, Constantine, Algérie.
[2] Institut de l’Evaluation Environnementale et de la Recherche sur l’Eau (IDAEA), Conseil Supérieur de la Recherche Scientifique (CSIC), Barcelone, Espagne.

Anthropogenic sources are also responsible for particulate pollution; farming activities using fertilizers and pesticides, industry with the various pollutants it rejects, petroleum refining, combustion and finally road transport (Lamaison 2006; Tombette, 2007; Han et al., 2006). According to the IUPAC definition, MTE (metallic trace elements) is: "Anything with an average concentration below 100 ppm." The term "ultra-trace" is a name that has no strict definition, but which is frequently used in the literature (Brown & Milto, 2005). MTE are part of air pollutants and their determination in the fine particles is an important parameter in the assessment of the health risk induced by these particles (Perez et al., 2004). Recent studies have developed methods for the determination of harmful MTE such as: Cd, Co, Cr, Cu, Ni and Pb present in aerosols (Castillo et al., 2008; Moreno et al., 2006). Analysis of MTE present in dust samples taken from the ambient air at very low concentrations is a challenge. The low weights of the samples increase the risk of loss and contamination. Research has mainly focused on the development of new methods to increase the sensitivity and selectivity of the analysis of trace elements. Direct methods include X-ray fluorescence (XRF), X-ray emission induced by proton (PIXE) analysis and instrumental neutron activation (INAA). However, matrix effects can cause major interferences while using these techniques. The most common methods used today for the determination of metallic elements in environmental samples involve highly sensitive spectroscopic techniques, such as atomic absorption spectroscopy (FAAS, ETAAS), inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectrometry (ICP-MS and ICP-AES). The use of these techniques requires dissolving the samples before the determination of the metal contents. In recent years, analysts have recognized increasingly that most systematic errors could be introduced during the sampling and sample preparation steps. Currently, the influence of the sample preparation step on the quality of the analysis results is recognized worldwide (Ehi-Eromosele et al., 2012). Different digestion methods for trace metals present in aerosols can be used. The extraction efficiency depends on several factors: the sample nature and its matrix, the time available for analysis and the optimal time of acid digestion (Ehi-Eromosele et al., 2012).

In the scientific literature, several extraction protocols of trace elements in aerosols are reported without specifying whether the type of extraction is exhaustive allowing the total dissolution of metals or selective for a specific metallic fraction. Several techniques are used for the extraction of metal elements contained in solid environmental matrices (aerosols, sediments, soil, marine and dust samples). Some studies are based on the extraction in a single step 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, etc. (Pérez et al., 2004; Petterson & Olsson, 1998; Ragosta et al., 2008; Bettinelli et al., 2000). Other studies implement the sequential extraction based on the principle of the attack of the sample by gradually stronger mineralizing solutions (Grotti et al., 2002; Ryan et al., 2008; Jimoh, 2012). A total digestion method must include the use of hydrofluoric acid HF which, despite its harmful health effects, remains the only reagent capable of releasing the silicates bound metal fraction. However, in many studies, other techniques such as aqua regia proved equally effective for some metals (Sastre et al., 2002).

The purpose of this study is to conduct a comparative study between a total digestion technique (HF / HNO_3 / $HClO_4$) and two partial extraction techniques (HNO_3 / HCl) and (HNO_3 / HCl / H_2O_2) to measure the efficiency of such techniques towards the metallic elements: Cd, Co, Cr, Cu, Ni and Pb.

2 Material and Methods

2.1 Samples

A standard material (UPM 1648 Fly Ash) and ten PM10 quartz fiber filters were used for sampling PM10 in the period between 15/01/2015 and 13/03/2015 at the Slimane Zouaghi campus of the university of Constantine using a high volume sampler, model Tisch-TE-6001 (Fig. 1).

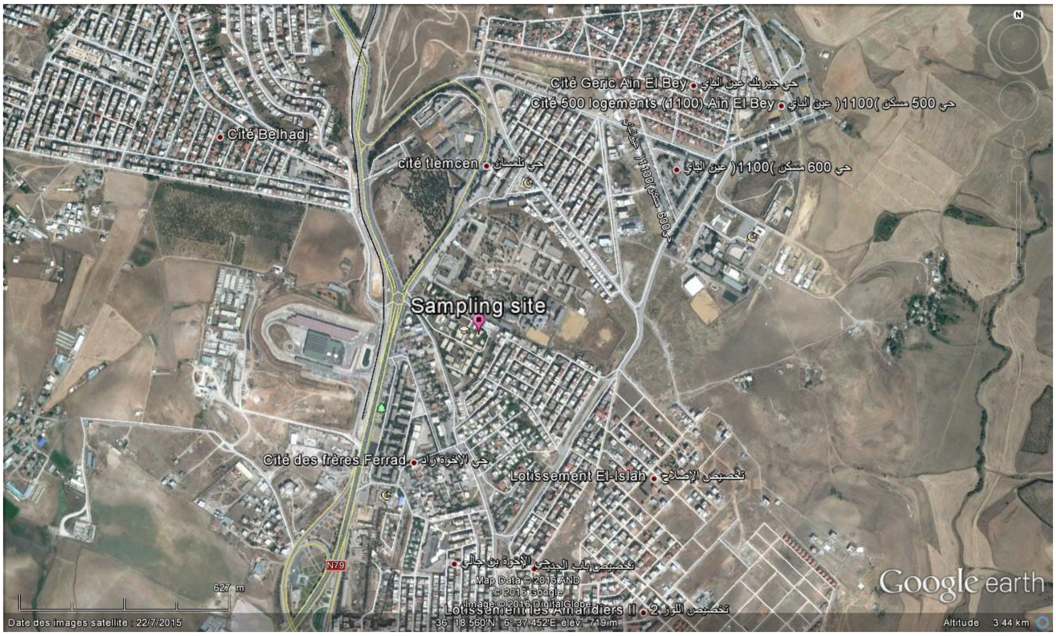


Figure 1: Map of PM10 sampling site

2.2 Dust mineralization

Experimental protocols used for PM10 sample dissolution are shown below. To complete each extraction protocol, circular 30 mm diameter discs were cut from the ten PM10 filters.

2.2.1 First Protocol (P1)

Samples were digested in a solution containing 1 ml HNO_3 and 2 ml HF in a closed PFA bottle at 90 °C for at least 8 hours. After cooling, the containers were opened and 1 ml of $HClO_4$ was added. The acids were then completely evaporated by placing the PFA containers on a hot plate at 240 ºC. The remaining dry residue was dissolved with 2.5 ml of HNO_3 before being diluted with distilled water (MilliQ) to 25 ml, to obtain solutions of 10% HNO_3 that were centrifuged for 20 minutes at 3000 rpm (Querol et al., 2001).

2.2.2 Second Protocol (P2)

The samples were introduced into PFA vials. A 10 ml solution of a (3:1) mixture (12M HCl and 17M HNO_3) was left at room temperature for 24 h. Then the solution was digested on a hot plate at 130 °C for 15 min. After cooling at room temperature, the suspension was filtered and diluted to 25 ml with 0.17 M HNO_3 (Pena-Icart et al., 2011).

2.2.3 Third Protocol (P3)

The extraction of the filters was carried out using the following reagents: HCl (37%), H_2O_2 (35%) and HNO_3 (65%). Samples were put in a PFA flask and a solution containing 30 ml HCl and 5 ml H_2O_2 was added. After heating for 1 hour on a hot plate at 120 °C, the solution was filtered and 20 ml HCl (1+1) were added to the residue for 15 min to complete the extraction. The PFA flask content was filtered again and the filtrate was added to the filtrate of the previous step. The solution was concentrated on a hot plate until a small volume was left in the flask. The latter was then transferred to a volumetric flask of 25 ml. This volume was filled up with a HNO_3 solution (2+98) (Awan et al., 2011).

2.2.4 Analytical techniques

The resulting solutions were then analyzed by ICP-AES (IRIS Solutions Advantage Thermo TJA) for elements, Zn and Mn and by ICP-MS (X Series II Thermo) for elements Cu, Pb, Co and Ni.

3 Results and Discussion

3.1 Evolution of PM10 concentrations

Ten PM10 samples were collected during from 15/01/2015 to 13/03/2015. The daily concentrations of PM10 are shown in Fig. 2.

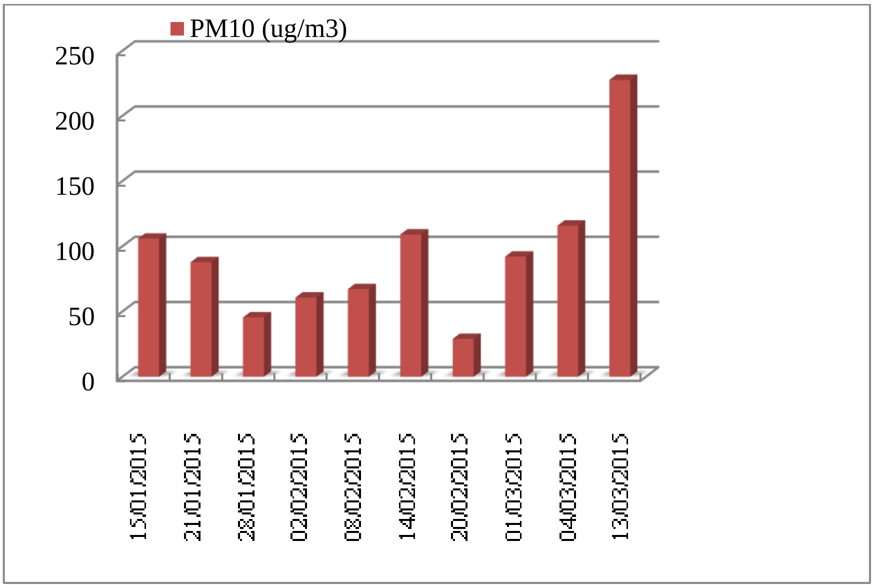


Figure 2: Daily atmospheric levels of PM10

Table 1 summarizes the results for PM10.

Table 1: PM10 concentrations measured at the study area

Number of samples	10
Sampling period	15/01/2015 - 13/03/2015
Unit	µg/m^3
Average daily concentration	94
Maximum daily concentration	227
Minimum daily concentration	28

PM10 concentrations range from 28 µg/m^3 to 227 µg/m^3 with an average value of 94 ug/m^3. The results obtained show that daily levels of PM10 vary widely. This variation is linked both to fluctuations in the intensity of emission sources (road traffic, various industrial activities) and to natural influences (desertic sand, biomass fires, dust resuspension) and weather parameters (wind direction and intensity, humidity, precipitation, temperature) (Kerbachi et al., 2009).

3.2 Concentrations of the standard material (P1633b) bound metal elements extracted according to the three extraction protocols

The most common approach for measuring the efficiency of digestion procedures is the estimation of the percentage recovery of metals contained in standard materials having a composition and a structure similar to those of the samples (Celo et al., 2010). Table 2 shows the certified values and reference values of the six studied metallic elements contained in the standard material (P1633b) and the measured concentrations obtained after analysis of the same material using the three extraction protocols.

Using the data from Table 2, we calculated the percentage recovery of each metal element and for each extraction protocol. The results are shown in Table 3.

Table 2: Certified values and reference values and measured concentrations for Cu, Pb, Zn, Co, Mn and Ni contained in the standard material (P1633b)

Element	Certified and reference values	Measured concentrations		
		P1	P2	P3
Cu (mg/kg)	113	102	47	68
Pb (mg/kg)	68	58	31	37
Zn (mg/kg)	210	266	123	173
Co (mg/kg)	50	40	17	24
Mn (mg/kg)	131,8	137	65	81
Ni (mg/kg)	120	130	44	59

Table 3: Percentage recovery of metal elements contained in the standard material (P1633b)

R%	P1	P2	P3
Cu	90%	42%	60%
Pb	85%	46%	54%
Zn	127%	59%	83%
Co	80%	34%	48%
Mn	104%	49%	61%
Ni	108%	37%	49%

In order to interpret the observed differences between the three extraction techniques, it is essential to define the metallic fraction targeted by each extraction method. The mixture HF / $HClO_4$ / HNO_3 (P1) allows the determination of the total contents of the analyzed elements (Bettineli et al., 2000). The aqua regia extraction method (P2) is a technique that is frequently used for the extraction of metals in different environmental matrices. This technique solubilizes most of the residual minerals (Bettineli et al., 2000). The addition of oxygenated water in the third solution (P3) makes it possible to solubilize the oxidizable phase metals such as sulphides and organic matter (Grotti et al., 2002).

The extraction efficiency is relatively better for method P3 compared to method P2 for all studied elements with percentage recoveries ranging from 48% to 83% for P3 and from 34% to 59% for P2. The addition of H_2O_2 in method P3 improved the percentage recoveries by 18% for Cu, 8% for Pb, 24% for Zn, 14% for Co, 12% for Mn and Ni.

The addition of HF in the first extraction protocol P1 improved significantly the extraction efficiency for all elements with percentage recoveries ranging from 85% to 127%. This method improved the percentage recoveries achieved by protocol P3 by 50% for Cu, 31% for Pb, 32% for Co, 39% for Mn and 51% for Ni, considering that percentage recoveries cannot exceed 100%. The overestimated observed Zn concentration was due to possible contamination.

3.3 Concentrations of the metal elements contained in aerosols and obtained according to the three extraction protocols

Figure 3 allows a comparison between the mean concentrations of six metallic elements present in the solutions obtained by the three extraction protocols for ten PM10 samples represented by: S1, S2, S3, S4, S5, S6, S7, S8 S9 and S10.

P1 allows the highest extraction efficiency of the three digestion methods for the elements determined, in most individual samples. Exceptions concern Pb contained in samples S3 and S8, Ni contained in samples S1, S3, S8 and S10 and Zn contained in samples S3 and S10. This may be due to possible contamination of the samples while performing protocols P2 and P3.

P2 and P3 protocols are two partial extraction techniques. The absence of HF in the P2 and P3 reagent mixtures does not allow the release of the metal bound silicate fraction (Hong et al., 2005). This fraction varies from one sample to another depending on the element considered and this explains the significant difference in extraction efficiency between the total extraction protocol P1 and the two partial extraction protocols P2 and P3. Both protocols present a more or less similar efficiency for elements Mn, Ni and Co. Protocol P2 is on average more efficient than P3 protocol for the extraction of Cu and Zn.

The behavior of Pb is exceptional with concentrations very close to each other for protocols P1, P2 and P3 for almost all samples. This element has a high affinity for organic matter (Mathews et al, 2012). The organic fraction may well be completely dissolved by the various mixtures used in the three digestion methods.

For sample S7 which shows the minimum PM10 concentration, significant differences were not found in the amounts of metal elements extracted by the three digestion methods in each studied sample.

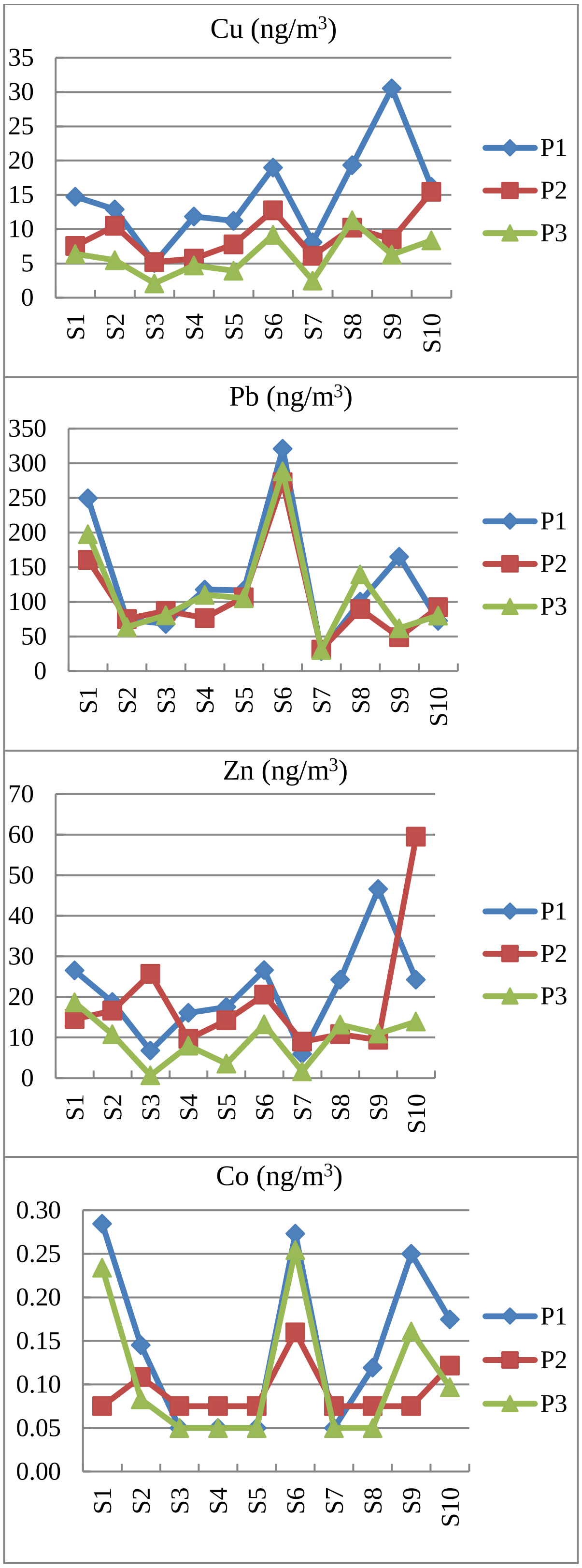
3.4 Comparison of the results obtained for the standard material (P1633b) and PM10 samples

The efficiency of an extraction technique can only be quantified by using standard samples having certified values and reference values for the elements of interest because these materials are easier to analyze than real environmental samples (Gerboles et al., 2011). Therefore, such standard samples can not confirm the digestion efficiency of real samples because of different inherent matrices and element concentration ranges (Celo et al., 2010). Figure 4 compares the concentrations of metal elements extracted by the three extraction methods on standard material and the average concentrations of the same elements contained in the ten studied PM10 samples.

For Pb, Zn, Co, and Mn and despite the different concentrations ranges between samples and between samples and the standard material, the same findings apply for the three extraction protocols for the standard material (P1633b) and for the studied PM10 samples. The extraction efficiency increases in the order P2, P3, P1.

The total digestion method P1 is most efficient for the six elements analyzed in both the standard material and the studied PM10 samples.

The addition of H_2O_2 in the third method has improved the percentage of recovery of all elements contained in the standard material (P1633b) in comparison to the second extraction method. However, the average concentrations of Cu, Zn and Ni contained in the PM10 samples are higher when they are extracted by method P2 in comparison to method P3. This could be explained by the difference in composition of the samples studied in both cases.


Cu (ng/m3)
35
30
25
20
15
10
5
0
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10
P1
P2
P3
Pb (ng/m3)
350
300
250
200
150
100
50
0
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10
P1
P2
P3
Zn (ng/m3)
70
60
50
40
30
20
10
0
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10
P1
P2
P3
Co (ng/m3)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10
P1
P2
P3

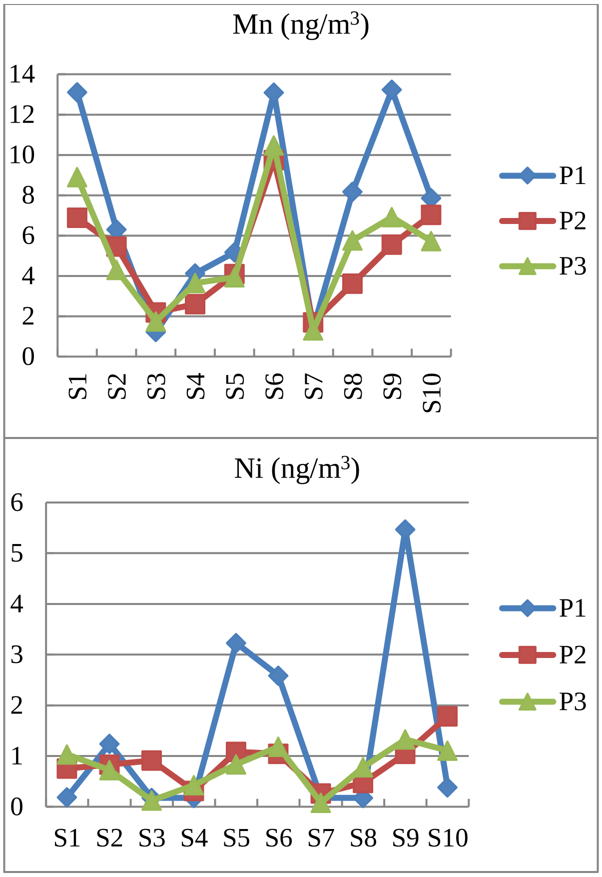


Figure 3: Comparison of the concentrations of Cu, Pb, Zn, Co, Mn, and Ni extracted from PM10 by the three digestion methods

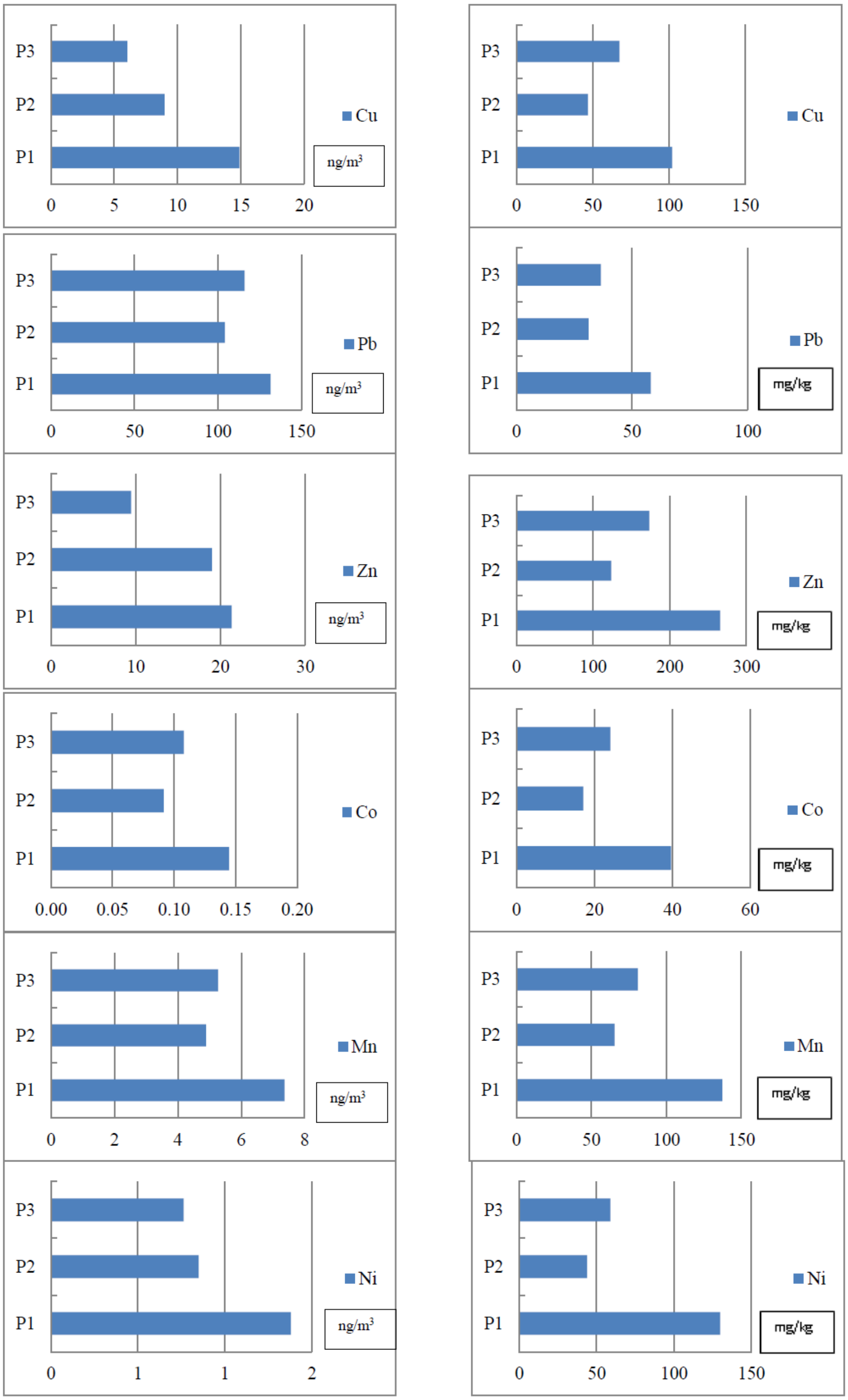


Figure 4: Comparison of the concentrations of metal elements extracted from the PM10 samples (left) and the certified material P1633b (right) by the three digestion methods

4 Conclusion

This study highlights the different metal extraction capacities of three digestion methods. Extraction efficiencies were shown to vary greatly between these methods. This emphasizes the need for normalization of digestion methods in order to be able to harmonize results for comparison purposes.

The addition of H_2O_2 to aqua regia has improved the percentage of recovery of all elements contained in the standard material (P1633b). Such an improvement concerned only Co and Mn and to a lesser extent Pb. Extraction of Cu, Zn and Ni in PM10 samples was better with aqua regia. The silicate phase could be poorly attacked by the solvents used with respect to some elements. Mn oxides and hydroxides which are not completely dissolved by aqua regia could explain the small amount of extracted Mn.

The total digestion method proved to be the most efficient for extracting Cu, Pb, Zn, Co, Mn and Ni in a standard material and in ten PM10 samples. No reagent mixture can replace the presence of HF which, despite its harmful effects, is the only reagent capable of releasing the metal fraction associated with silicates. Significant differences between extraction protocols vary with samples, matrices and elements. The efficiency of an extraction technique depends on several factors: the extraction solution, the nature of the sample matrix, the analysis time available as well as the optimal time of digestion acids (Ehi-Eromosele et al., 2012).

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