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Influence of filters, solid to fluid ratios and matrices on the bioaccessibility of potentially toxic elements in airborne PM

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Abstract

Determination of bioaccessibility of potentially toxic elements in inhaled airborne particulate matter have brought the attention of researchers. In this study, effect of filters and solid to fluid ratios on the bioaccessible fraction of elements in airborne particulate matter determined by simplified bioaccessibility extraction test were investigated. A matrix matched and a non-matrix matched set of calibration standards for inductively coupled plasma mass spectrometry were also examined. Nine elements: As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined. Results obtained illustrated that matrix matching was necessary for preparing As calibration standards. Results also indicated that the ratio adopted in miniaturized version of the simplified bioaccessibility extraction test (0.1 g:10 mL) is the best choice when all elements tested are to be measured, compared to other ratios investigated in this study. However, all ratios can be applied with no significant difference for Cd, Cu, and Ni. Results from filters' effect demonstrated that the relative percent difference between bioaccessible fraction of elements in soil only and in soil loaded on filters was less than 20% for all elements except for Cd, Ni, and Zn. Discrepancies observed for Zn were due to the variability in its amount used to produce filters.

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Keywords: Bioaccessibility; SBET; airborne PM; Potentially toxic elements; Solid to fluid ratio; Matrix

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1. Introduction:

Potentially toxic elements (PTE) are considered one specific constituents of airborne particulate matter (PM) that cause adverse effects on human health, particularly those associated with lung cancer [1-3]. Inhalation is a route by which the PTE could be transferred to humans [4]. The PM_{10} (i.e. PM $\leq$ 10 μm) is the aerodynamic diameter of airborne PM that can be inhalable.[5-7] The small size of those particles makes them to be more loaded with contaminants than the other particles because of its high surface-to-mass ratio [8]. When those particles are inhaled, the majority of those are mucociliary cleared and transported to gastrointestinal tract where they are ingested [7, 9, 10].

The considerable health risk of PTE in ingested material is related to the fraction that is soluble in the gastrointestinal tract and available for absorption [11]. Bioaccessibility testing is a method that determine the soluble portion of ingested PTE that would be available for absorption [12, 13]. It has been recently applied to study airborne PM in vicinity of coal-fired mineral processing industries in India [14], mine tailing in Mexico [15], outdoor dustfall [16], arid areas [17], and urban sandstorm contamination in China [18], urban and an industrial area in Spain [19], urban areas in Italy [20], and dust of an iron mining and industrial complex in Iran [21].

As the majority of inhaled PM_{10} is finally accumulated in the gastrointestinal tract, oral bioaccessibility tests can be used to estimate the bioaccessibility of PTE in PM. Many *in vivo* and *in vitro* methods have been developed to determine the oral bioaccessibility of elements in soils, particularly focused on As and Pb [22]. The *in vitro* methods are more commonly used compared to the *in vivo* methods because of their low-cost, replicability, and ease and short time to implement [23]. The simplified bioaccessibility extraction test (SBET) is a popular one step oral bioaccessibility method (i.e., stomach phase only) which has been broadly used [22, 24-26]. This is because of its simple reagents and rapidity [27]. Its digestive fluid consists of a 0.4 M glycine solution adjusted at pH 1.5 ± 0.05 by hydrochloric acid [28].

During the first quarter of this century, few studies were conducted to apply the SBET to PM [23, 28, 29], and only one study investigated the bioaccessibility of PTE in PM loaded on FDMS filters that were used in routine air quality monitoring [28]. In this study, the original SBET method was

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miniaturized to be applicable for PM_{10}. However, this method need to be validated for other reference materials representing airborne PM, as well as the effect of solid to fluid ratio was not investigated for this version of the SBET.

The aim of the present study was:

(a) To validate the miniaturised version of the SBET by using different reference material.
(b) To optimise the miniaturised version of the SBET methods by investigating the effect of solid to fluid ratio and study of the matrix matched effect.

2. Materials and Methods

2.1. Apparatus and Reagents

Glassware and plastic-ware were overnight soaked in 10% nitric acid (v/v) and then completely washed three times using distilled water. After rinsing them with deionized water, they were air dried. Blank Pallflex TX40 FDMS filters, supplied by Air Monitors Ltd., Gloucestershire, UK, were used. Extracts were analysed by inductively coupled plasma mass spectrometer (ICP-MS) (Model 7700x, Agilent Technologies, Cheshire, UK). The reagents used were of analytical grade. Concentrated nitric acid (S.G. 1.42, 70% w/w, trace analysis grade) and glycine were obtained from Fisher scientific (Loughborough, UK). Concentrated hydrochloric acid (analytical specification, 36.5-38% w/w) was purchased from Sigma-Aldrich (Gillingham, UK). Multi-element calibration standard solutions for ICP-MS were prepared using a multi-element standard stock solution (10 mg L^{-1} of As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn) and Fe standard stock solution (1003 mg L^{-1}) obtained from Qmx Laboratories, Essex, UK.

2.2. Procedures

2.2.1. Selection of calibration standard for ICP-MS

Two groups of calibration standard solutions were prepared using five solutions for each group. To set the concentrations of the first group, different calculated volumes from the multi-element standard stock solution and the Fe standard stock solution were placed into a 25 mL volumetric flask then made up using a 1% (v/v) nitric acid solution (see Table 1). The same volumes from the multi-element standard stock solution and the Fe standard stock solution were put into different 25 mL volumetric flasks then made up to mark with the 0.4 M glycine solution. Solutions obtained were stored in polyethylene bottles in the fridge at 4 °C prior to analysis by ICP-MS.

2.2.2. Solid to fluid ratio

To investigate the effect of solid to fluid ratio on the measured bioaccessible concentration of PTE, five ratios with different volume of glycine, 0.1 g:20 mL, 0.1 g:30 mL, 0.1 g:40 mL, 0.1 g:50 mL, 0.1 g:100 mL were investigated and compared with values obtained from a ratio of 0.1g:10 mL applied in miniaturised version of the SBET and the ratio of the original procedure of the SBET (i.e. 1.0 g:100 mL) mentioned in ref [28]. The BGS guidance material (BGS102 from British Geological Survey, Keyworth, UK) was used for this procedure.

2.2.3. The efficiency of SBET to extract PTE from soil loaded on FDMS filters

The soil samples and the loaded filters as well as a blank filter were subjected to a miniaturised SBET as detailed in ref [28]. A Glasgow urban soil reference material (URM) sampled during the EU URBSOIL project (contract EVK-CT-2001-00053) was used for this procedure. It had been sieved through a 100 µm sieve representing the fraction of urban particulate matter that can be airborne. Obtained extracts were stored in polyethylene bottles in the fridge at 4 °C prior to analysis by ICP-MS.

2.3. Analysis of extracts

The ICP-MS system (model 7700x, Agilent Technologies, Cheshire, UK) was used to determine concentrations of elements according to the operation conditions tabulated in Table 2. A constant amount of sample at a rate of 1 mL min^{-1} was introduced using an auto-sampler and a peristaltic pump. Indium isotope, ^{115}In, was used as an internal standard, and the collision cell mode was operated. The computer software (ICP-MS Mass Hunter 4.1 Workstation software) was used to process the data.

2.4. Quality control

Analytical performance was assessed by processing triplicate samples (% RSD) and by use the relative percent difference (RPD). In addition, the student t-test (at 0.05 significance level) was conducted.

3. Results and discussion

3.1. Selection of calibration standard for ICP-MS

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It was necessary to determine whether ICP-MS standard calibration solutions needed to be reagent matched, as is usual in analytical science, or whether 1% HNO_3, as recommended by USEPA [30] could be used to avoid introduction of glycine to the instrument. Table 3 shows the slope and detection limit for calibration standard solutions prepared by 1% HNO_3 and 0.4 M glycine for ICP-MS. Based on %RPD, there was no significant difference between the values of slope with HNO_3 and glycine for all elements tested except for As. Here, the RPD was 64.8%, while it ranged from 1.1 to 5.3 for the remainder of elements. The difference between As slopes may be due to its high ionization potential (IP)(first IP 9.8152 V), the formation of polyatomic ion ($^{40}Ar^{35}Cl$) and signal suppression with HNO_3. So, matrix matching should be used when the calibration standard solutions for As are prepared, whereas the use of non-matrix matched calibration standards can be used for the remainder of elements.

The obtained results show that the detection limit with HNO_3 is lower than with glycine, therefore calibration with HNO_3 may be preferred over glycine (except for As, see Figure 1), if samples have low concentrations of elements. These results agree with the conclusion of a study conducted by Falciani *et al.*, 2000 [31] regarding As and some elements, but they do not agree about Cd and Zn (see Figure 1) where the study illustrated that a matrix matched was required for preparing the calibration standard solution. The improvement for Cd and Zn in the current study may be due to developments in the methods and techniques used to overcome interferences in ICP-MS, particularly spectral overlap, by using for example collision cells.

3.2. Solid to fluid ratio

Figure 2 shows the bioaccessible concentration of PTE in BGS 102 using the original procedure of the SBET and the miniaturised procedure with six different solid to fluid ratios (0.1 g:10 mL, 0.1 g:20 mL, 0.1 g:30 mL, 0.1 g:40 mL, 0.1 g:50 mL, 0.1 g:100 mL). According to student t-test (at 0.05 significance level), (see Table 4) there was a significant difference (i.e., t-test failed) between the bioaccessible values of As, Cr, Fe, and Pb obtained from the original procedure and those obtained from all ratios, except for 10- and 20-mL volume of glycine. For the 0.1 g:20 mL ratio, a significant difference was observed for Fe and Mn, whereas the t-test was passed for all bioaccessible values of PTE when 0.1 g:10 mL ratio was applied. The results of %RPD (see Table 4) show that values were > 10 % for As, Cr, Fe, Pb, and Zn when all ratios were applied, except for the 0.1 g:10- and 20-mL ratios. The %RPD values were <10% for As, Cr, Cu, and Pb and between 10.3% and 18.8% for other PTE when the ratio was 0.1 g:20 mL, whereas, for the 0.1 g:10 mL ratio, it was less than 10% for all

PTE tested, except for Fe (17.5%) and Pb (13.7%). Recoveries respect to the original procedure (see Table 4) were between 111% and 171% for As, Cr, Fe, Pb, and Zn when all ratios investigated were applied, except 10- and 20 mL volume of glycine. The good recoveries (100 ± 10%) were shown for As, Cd, Cr, Cu, and Pb, and between 85.1% and 121% for other PTE when the 0.1 g:20 mL ratio was applied. For the 0.1 g:10 mL ratio, all recoveries were within (100 ± 10%), except for Fe (119%) and Pb (115%). For Cd, Cu, and Ni, there was no significant difference (t-test passed) between all ratios investigated and that adopted in the original procedure, and the values of the %RPD and the recoveries were less than 11% and within (100 ± 10.3%), respectively.

3.3. The efficiency of SBET to extract PTE from soil loaded on FDMS filters

Table 5 shows the bioaccessible concentrations of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, respectively in soils smeared on FDMS filters and in soils only. Relative standard deviation (%RSD) values for bioaccessible PTE concentration in soils alone were between 2.11 and 10.5% (see Table 5) and that indicates a good precision of the analytical method. However, %RSD values ranged from 4.70 to 20.9% for bioaccessible PTE concentration in soils smeared on FDMS filter and that may be because the smearing method used when loading the FDMS filters lead to some variability.

Results obtained demonstrated that the highest value of bioaccessible concentration was for Fe (2135 mg kg^{-1}), whereas bioaccessible Cd concentration was the lowest (0.206 mg kg^{-1}) (see Table 5). This could be related to values of pseudototal content of these elements [32]. However, this relation was not observed with other elements tested. One such example, bioaccessible Cu concentration in soils alone (39.8 mg kg^{-1}) was larger than bioaccessible Zn concentration (14.8 mg kg^{-1}), though pseudototal content of Zn in soils alone (177 mg kg^{-1}) was larger than pseudototal of Cu (111 mg kg^{-1}) [32]. This may be because of the numerous binding sites that might respond differently to a change in the pH of the extractant, and may be because of other factors such as oxidation state and sources of PTE in soils. Bioaccessible Cr concentration obtained in this study (3.60 mg kg^{-1}) was nearly in the range of values obtained from a study conducted on soils collected from Glasgow city centre, and these values were between < 3 and 3.9 mg kg^{-1} in the simulated stomach fluid (pH= 1.2) of the UBM [33].

Bioaccessible PTE concentrations in blank FDMS filters were generally, as expected, very low except for Zn (see Table 6). They ranged from 0.0004 µg per filter for As to 0.311 µg per filter for Fe, but the value for Zn was 4.36 µg per filter. This could be because of the low values of pseudototal content of PTE in blank FDMS filters, except for Zn and Fe [28]. Bioaccessible Cr and Cu concentrations were less than values of detection limit.

To study if there is significant difference between the values of bioaccessible PTE concentration in soils alone and those in soils loaded on FDMS filter, F-test, t-test, and %RPD were applied (see Table 7). Statistical results obtained based on the F-test refer that there was no significant difference between a standard deviation of bioaccessible PTE concentrations in soils in the presence of FDMS filter and a standard deviation of bioaccessible PTE concentrations in soils in the absence of FDMS filter except for Zn. In addition, and based on the t-test and the %RPD, there was no significant difference between the mean bioaccessible PTE concentration in soils loaded on FDMS filters and in soils alone except for Cd, Ni, and Zn. For Zn, these exceptions may be because that the blank FDMS filters contain different concentrations of Zn [28], whilst for Cd and Ni, the significant difference could be because of soils homogeneity or the smearing method of the FDMS filter.

4. Conclusion

The effect of filters, solid to fluid ratio, and matrices were investigated for measuring bioaccessible fraction of PTE in PM by the SBET. Results obtained from an experiment of matrix-matched and non-matrix matched calibration standard for ICP-MS demonstrated that the non-matrix matched calibration standard can be used for all elements tested except As, where matrix-matched calibration standard should be used. In practice, since multi-element standards were used, this means that all calibrants were reagent-matched. Outcomes of this study shows that there was no effect of solid to fluid ratio on the bioaccessible concentration of PTE in airborne PM when the SBET was used to determine Cd, Cu, and Ni. However, for other PTE tested, reducing the original ratio of the SBET to 10-fold should be adopted, as with other ratios investigated, the measurement could be underestimated or overestimated. Statistically, there was no significant difference between the values of PTE concentrations measured in soils loaded on FDMS filters and those determined in soils in the absence of FDMS filters except for Cd, Ni, and Zn. In summary, the miniaturised version of the SBET was successfully validated and optimised to be used for determination of PTE tested in airborne PM. The developed method could be applied not only to outdoor urban airborne particulates but also, in other scenarios where material is collected on filters, for example workplace occupational health monitoring, provided care is taken to first assess any PTE contribution from blank filters.

Acknowledgement

JA acknowledges financial support from the Iraqi Ministry of Higher Education and Scientific Research.

Conflict of Interest

Author declares that there is no conflict of interest.

Data availability statement

Authors confirm that the data supporting the findings of this work are available within the article.

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Legends for Figures

Figure 1: The calibration curves of ICP-MS for As, Cd, and Zn using 0.4 glycine and 2% HNO_3 for preparing standard solutions.

Figure 2: Measured bioaccessible concentration of PTE in BGS 102 using the original procedure of the SBET (100 mL ORG) and the miniaturised (MIZ) procedure with six different solid to fluid ratios (0.1g to 10 mL, 0.1 g to 20 mL, 0.1 g to 30 mL, 0.1 g to 40 mL, 0.1 g to 50 mL, 0.1 g to 100mL).

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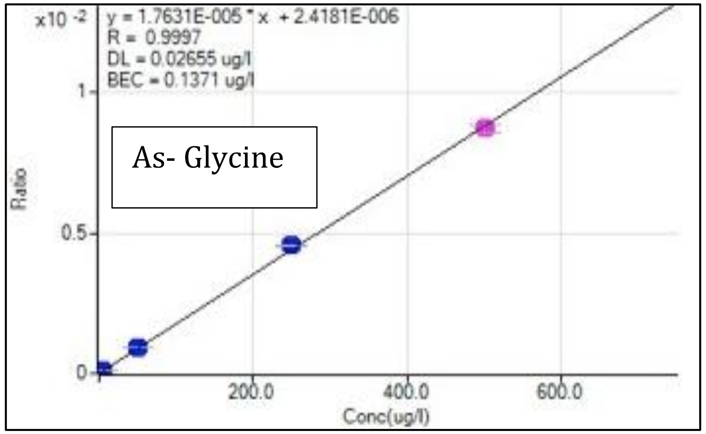

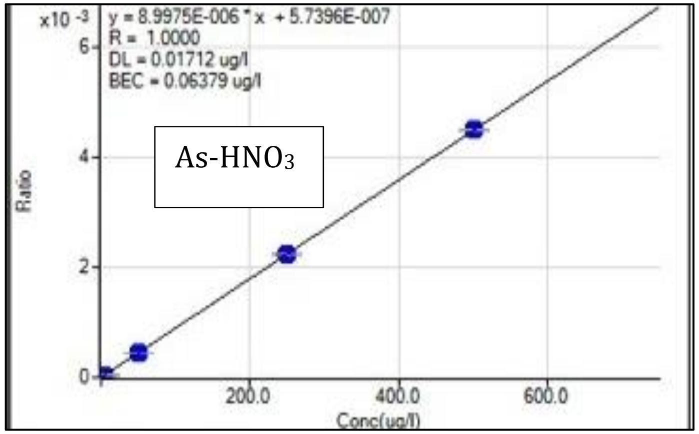

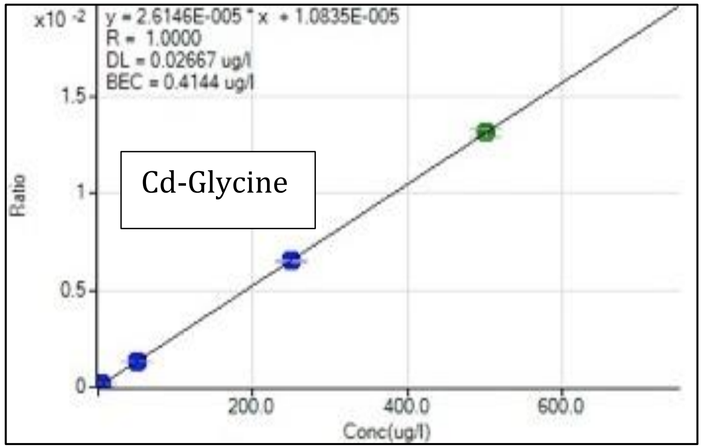

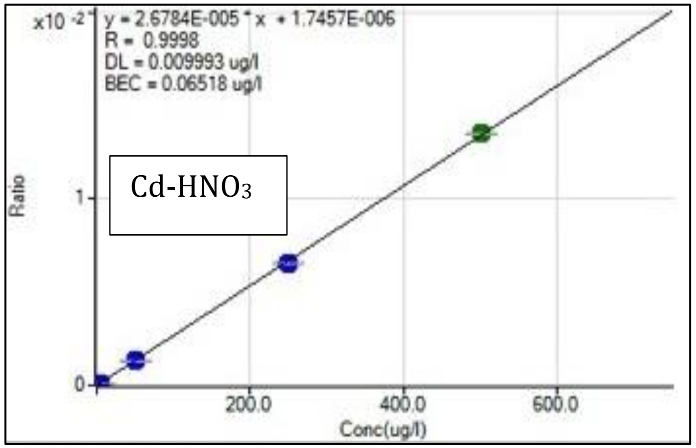

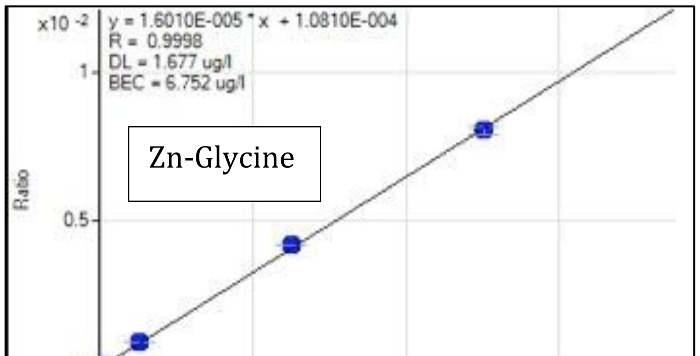

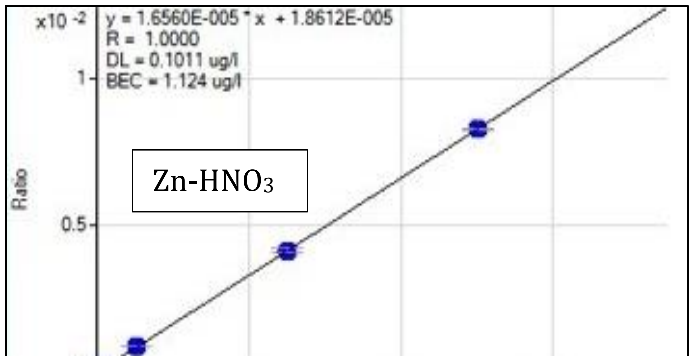

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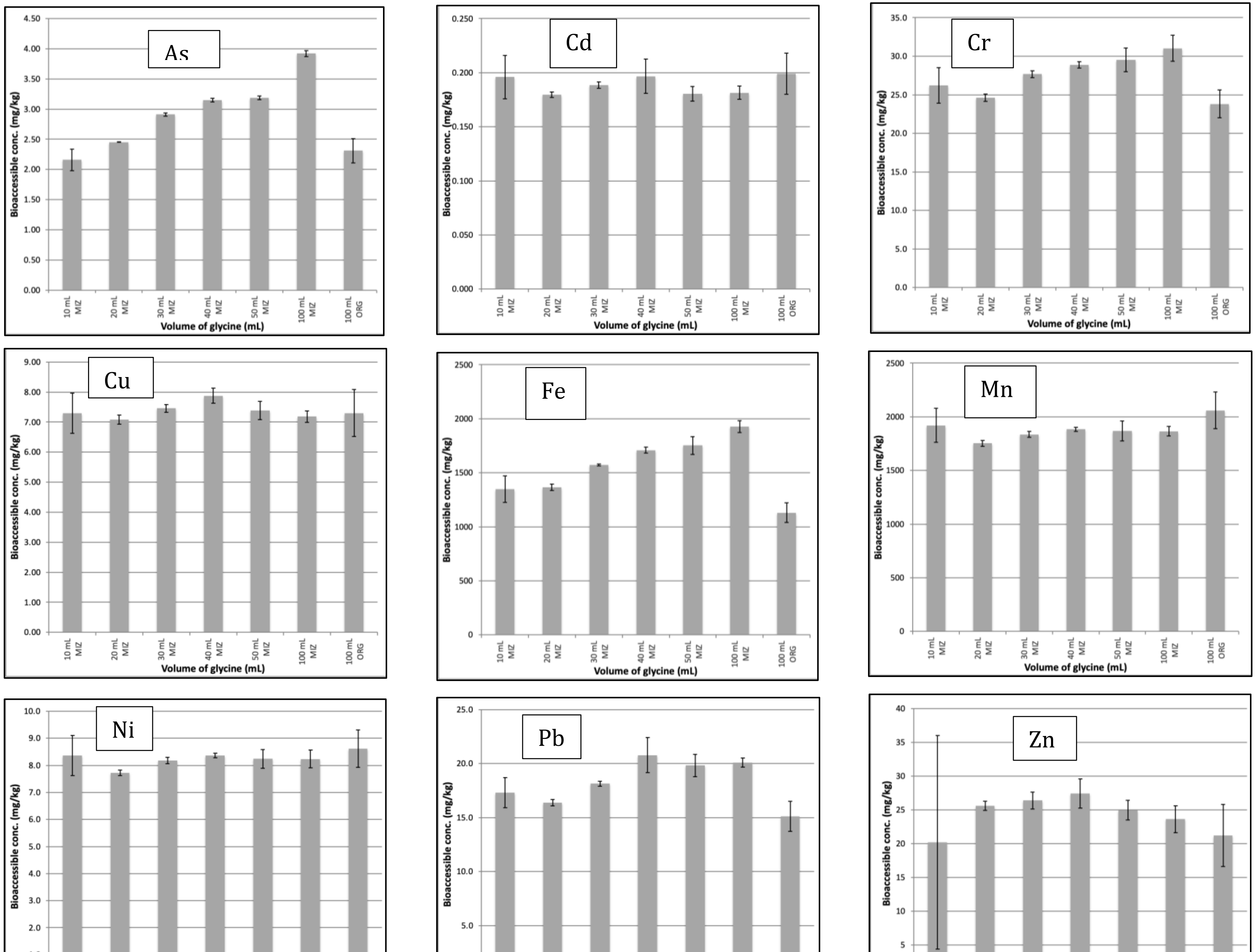

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Table 1: The ICP-MS Calibration standard solutions.

Standard	Fe standard stock		Multi-element standard stock	
	Volume (µL)	Concentration (µg L^{-1})	Volume (µL)	Concentration (µg L^{-1})
1	0	0	0	0
2	8	320.96	12.5	5
3	80	3209.6	125	50
4	400	16048	625	250
5	800	32096	1250	500

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Table 2: Operation conditions for the ICP-MS

Operation conditions	
Power (watt)	1550
Quadrupole bias (v)	-15
Octupole bias (v)	-18
Nebulizer gas flow (L min^{-1})	0.85
Plasma gas flow (L min^{-1})	15
Auxiliary gas flow (L min^{-1})	0.9
Collision cell gas (L min^{-1})	He (4.5)
Internal standard	^{115}In
Sample uptake rate (L min^{-1})	1

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Table 3: Slope and detection limit for calibration standard solutions prepared in 1% HNO_3 and 0.4 M glycine.

Analyte	Slope			D_L (µg/l)		R	
	HNO_3	Glycine	% RPD	HNO_3	Glycine	HNO_3	Glycine
^{75}As	9.00E-06	17.6E-06	64.8	0.0171	0.0266	1.0000	0.9997
^{111}Cd	2.68E-05	2.61E-05	2.4	0.0100	0.0267	0.9998	1.0000
^{114}Cd	6.43E-05	6.32E-05	1.8	0.00500	0.0232	1.0000	0.9999
^{52}Cr	8.95E-05	9.10E-05	1.6	0.00495	0.202	1.0000	0.9999
^{53}Cr	1.10E-05	1.11E-05	1.1	0.0519	0.225	1.0000	0.9999
^{63}Cu	1.03E-04	1.08E-04	5.3	0.00748	0.163	1.0000	0.9999
^{65}Cu	5.09E-05	5.36E-05	5.3	0.0377	0.286	1.0000	0.9998
^{56}Fe	8.06E-05	8.16E-05	1.2	0.102	1.54	1.0000	1.0000
^{57}Fe	2.05E-06	2.08E-06	1.5	0.720	2.42	1.0000	1.0000
^{55}Mn	5.51E-05	5.62E-05	1.9	0.0259	0.106	1.0000	0.9999
^{60}Ni	3.94E-05	4.04E-05	2.5	0.0211	0.0766	1.0000	0.9998
^{61}Ni	1.80E-06	1.83E-06	1.8	0.0612	0.147	1.0000	0.9999
^{206}Pb	1.06E-04	1.09E-04	3.0	0.0409	0.143	1.0000	0.9999
^{207}Pb	9.51E-05	9.82E-05	3.2	0.0696	0.158	1.0000	0.9999
^{208}Pb	2.26E-04	2.34E-04	3.6	0.0548	0.125	1.0000	1.0000
^{64}Zn	2.84E-05	2.75E-05	3.0	0.1665	0.636	0.9999	1.0000
^{66}Zn	1.66E-05	1.60E-05	3.4	0.1011	1.677	1.0000	0.9998

RPD: relative percent difference = $((|a1 - a2|)/((a1+a2)/2))\times100$; a_1: slope for HNO_3; a_2: slope for glycine; DL: detection limit; R: coefficient of determination.

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Table 4
Relative percent difference and recovery between bioaccessible concentrations obtained by the original and the miniaturized SBET with different solid to fluid ratio.

PTE	%RPD						Recovery (%)					
	Solid to fluid ratio (0.1 g to V mL)						Solid to fluid ratio (0.1 g to V mL)					
	10 mL	20 mL	30 mL	40 mL	50 mL	100 mL	10 mL	20 mL	30 mL	40 mL	50 mL	100 mL
As	6.44	5.94	**23.0^{F}**	**30.7^{F}**	**31.8^{F}**	**51.7^{F}**	93.8	106	**126**	**136**	**138**	**170**
Cd	1.41	**10.3**	5.43	1.15	9.79	9.18	99	90.2	94.7	98.9	90.7	91.2
Cr	9.68	3.40	**15.1^{F}**	**19.2^{F}**	**21.5^{F}**	**26.4^{F}**	110	103	**116**	**121**	**124**	**130**
Cu	0.138	3.07	2.11	7.62	1.17	1.56	99.9	97.0	102	108	101	98.5
Fe	**17.5**	**18.8^{F}**	**32.8^{F}**	**40.8^{F}**	**43.2^{F}**	**52.2^{F}**	**119**	**121**	**139**	**151**	**155**	**171**
Mn	6.98	**16.2^{F}**	**11.5**	**8.96**	**9.75**	**10.0**	93.3	**85.1**	**89.1**	91.4	90.7	90.5
Ni	2.74	**10.9**	5.13	2.94	4.39	4.49	97	**89.7**	95.0	97.1	95.7	95.6
Pb	**13.7**	8.14	**18.2^{F}**	**31.6^{F}**	**27.0^{F}**	**28.3^{F}**	**115**	108	**120**	**138**	**131**	**133**
Zn	5.25	**18.8**	**21.8**	**25.6**	**16.2**	**10.8**	95	**121**	**125**	**129**	**118**	**111**

RPD: Relative percent difference = $\{|a1 - a2|/((a1+a2)/2)\}\times 100$ *where a1: values in the original procedure and a2: values in in the miniaturized procedure; Recovery (%) = ([mean measured value in the miniaturized procedure]/[mean measured value in the original procedure]) × 100; F: means that the t-test (0.05 significance level) failed, without F means the t-test is passed.*

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Table 5
The mean bioaccessible PTE concentration in soil alone and in soil loaded on FDMS filters and %RSD values (n=3)

PTE	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Mean bioaccessible PTE concentration in soil alone (mg/kg)	2.74	0.206	3.60	39.8	2135	121	2.73	143	14.8
%RSD	5.54	2.11	4.62	10.5	4.56	2.19	4.51	2.82	2.64
Mean bioaccessible PTE concentration in soil on FDMS filter (mg/kg)	2.66	0.263	3.56	34.3	2152	141	3.54	159	28.5
%RSD	20.3	8.93	15.8	13.1	19.6	8.02	4.70	9.67	20.9

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Table 6
Bioaccessible PTE concentrations in blank FDMS filters.

PTE	**µg / filter Mean ± SD (n = 3)**
As	0.0004 ± 0.0001
Cd	0.0004 ± 0.0001
Cr	NC
Cu	NC
Fe	0.311 ± 0.073
Mn	0.010 ± 0.002
Ni	0.010 ± 0.005
Pb	0.030 ± 0.011
Zn	4.36 ± 0.86

NC: not calculated*; n: number of replicates; SD: standard deviation*

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Table 7
Tests of significance and % RPD for bioaccessibility of PTE in soils alone and soils loaded on FDMS filters.

Tests	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
F Calculated	12.6	33.1	11.5	1.16	18.7	18.2	1.82	14.5	234
F Critical (95%[a], 2[b], 2[c])	39.0	39.0	39.0	39.0	39.0	39.0	39.0	39.0	39.0
T Calculated	0.247	4.23	0.118	1.55	0.068	2.98	6.79	1.74	3.98
t Critical (95%[a], 4[d], 2[e])	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78	4.30
% RPD	2.96	24.3	1.12	14.8	0.47	15.3	25.8	10.6	63.3

a: significance level (α); b: $\nu_{numerator}$, where ν is a degree of freedom; c: $\nu_{denominator}$; d: ν for all elements except for Zn; e: ν for Zn; RPD: relative percent difference $=((|a1 - a2|)/((a1+a2)/2))\times 100$; a_1: bioaccessible PTE concentration in soil alone; a2: bioaccessible PTE concentration in soil on FDMS filter. A red coloured number indicates that a difference is significant.