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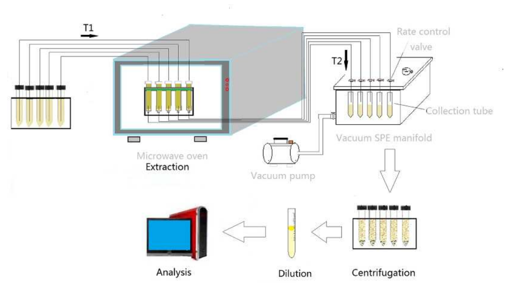

The approach combines the advantages of microwave and dynamic extraction technique, and up to five samples can be treated.

Multi-throughput dynamic microwave-assisted leaching coupled with inductively coupled plasma atomic emission spectrometry for heavy metal analysis in soil

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Abstract

A rapid and simple multi-throughput dynamic microwave-assisted leaching combined with inductively coupled plasma atomic emission spectrometry determination has been proposed for the simultaneous determination of Cu, Mn, Zn and Pb in soil. The approach combines the advantages of microwave and dynamic leaching technique, and up to five samples could be treated at the same time within 15 min. Nitric acid aqueous solution (20%, w/w) was employed as leachant at the flow rate of 1.5 mL min^{-1}. The leaching condition was optimized systematically and the leaching efficiencies were above 95% for Cu, Mn, Zn, Pb and lower for Cr, Cd, Ni and Co, compared to the conventional method. The leaching efficiencies of Cr, Cd, Ni, Co could be enhanced to above 60% when a soak progress was appended. Relative standard deviations of intra- and inter-day of Cu, Mn, Zn, Pb were in the range of

1.7–6.3% and 5.0–6.9%, respectively. The proposed method was more rapid than conventional digestion method and could be an alternative approach for the analysis of heavy metals in complex solid samples. The relatively closed system may have a broad prospect for leaching volatile elements, such as As, Se and Hg if combined with compatible detecting instrumentation.

Keywords: Dynamic microwave-assisted leaching, Soils, Heavy metals, Inductively coupled plasma atomic emission spectrometry

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1. Introduction

Heavy metal contamination is considered as one of the most important environmental issues. Heavy metals accumulate in soils due to their utilization in fertilizers, pesticides, plastic products, industrial wastes and mine area, etc.[1–4] The presence of heavy metals in soils may result in bioaccumulation in the food chain and cause serious problems to human health.[5–8]

Among the various analytical techniques used for heavy metal analysis, atomic absorption spectrometry (AAS),[9] inductively coupled plasma atomic emission spectrometry (ICP-AES)[10,11] and inductively coupled plasma mass spectrometry (ICP-MS)[12,13] are the most common techniques because of their good selectivity and sensitivity. The analysis of heavy metals in soil is a challenging topic, since the metals combined with high inorganic fraction in soil lattice are difficult to bring into solution for instrumental detection. Conventional wet digestion procedure which decomposes soils with aqua regia on a hotplate is time-consuming and tedious. The procedure has the loss hazard of volatile elements and high potential contamination to atmosphere due to the acid evaporation in the open system.[14,15]

Since the 1980s, microwave-assisted digestion (MAD) in closed vessels has been widely used due to its advantages over conventional procedures, including reduced loss risks, relatively less reagent and time consumption.[16,17] Many publications[16-19] have introduced the application of MAD to the digestion of heavy metals in soils, while the MAD procedure still has some drawbacks. Concentrated acids are still used during the procedure. When the digestion process is finished, the vessels must be cooled to room temperature before opening in case of danger. The digestion solution obtained needs to be treated with acid evaporation, centrifugation and filtration process before the subsequent determination, which lead to the complexity of the operation and cause the increase of sampling time and environment contamination due to acid evaporation. Hence, it is necessary to propose a new, rapid and eco-friendly preparation method for the analysis of heavy metals in soil.

Microwave-assisted continuous leaching [20] has been developed to leach cadmium and lead from leaves, as well as extractable arsenic from soils with sample throughput of not more than two, during which acid aqueous solution was used as leachant under microwave irradiation for 10–15 min.[21,22] Despite the advantages of minimal time consumption and simplification for sample preparation, the microwave assisted leaching techniques have the drawback of relatively low throughput compared to high-pressure MAD technique[23]. Dynamic microwave-assisted extraction (DMAE) of organic pollutants from soils has been developed coupled with other enrichment technique. [24] The DMAE can reduce the total analysis time and increase throughput of complex solid samples with simpler operation. But as far as we know, it has not been used to the leaching of heavy metals in soil.

In this work, we proposed a multi-throughput dynamic microwave-assisted leaching (MTDMAL) method combining the advantages of microwave[25] and dynamic leaching technique[26] with five soil samples treated simultaneously. The MTDMAL method has been successfully applied to the analysis of Cu, Mn, Zn and Pb in soils. The nitric acid aqueous solution was used as leachant, then the leachates were centrifugated and diluted before ICP-AES determination, instead of the cumbersome step of acid-evaporation, transfer, and filtration. The experiment parameters such as microwave power, kinds and concentrations of leachants, soil particle size and collection volume were optimized. As a consequence, the obtained contents of Cu, Mn, Zn and Pb in soils are comparable with those of conventional digestion procedure under the optimized conditions. The system may have a broad prospect for leaching volatile elements from soil, such as As, Se and Hg, if combined with compatible detecting instrumentation.

2. Experimental

2.1. Apparatus

An inductively coupled plasma atomic emission spectrometry (OPTIMA 3300DV, PerkinElmer, America) is equipped with a pneumatic nebulizer, a baffled Scott spray chamber, a quartz torch with a quartz injector tube (2 mm i.d.). The entire system was controlled by PE ICP Winlab software. The instrumental parameters were shown in Table 1.

The MTDMAL system represented in Fig.1 was assembled in our laboratory, which was modified based on our previous work.[24] The system was placed in the fume hood and consisted of a vacuum pump (HPD-25, Anlt, China), a vacuum SPE manifold (PN WA/T 058833, Waters, America), a centrifuge (SC-3610, Keda, China) and a flat countertop domestic microwave oven (EM720KG1-PW, Midea, China) with a maximum power of 750 W. The cylinder column (polypropylene, 66.0 mm height, 12.7 mm i.d.) with corresponding polyethylene sieve plates (aperture: 20 μm) was used as the leaching vessel (volume: 6 mL), which was static in the whole experiment process. The upper ends and the bottoms of the leaching vessels were connected with the leachant containers and the ports of the vacuum SPE manifold by tubes (T_1 and T_2) (polyethylene, 500.0 mm long, 0.5 mm i.d.), respectively (Fig. 1). The centrifuge tubes (polypropylene, 105.0 mm height, 28.5 mm i.d.) were used as containers of leachant and leachate.

2.2. Reagents and standards

Ultrapure water (18.2 MΩ·cm, Milli-Q system, Millipore, Billerica, MA, America) was used to prepare all the standard solutions and reagents. Quartz sand (0.710mm, G.R.), Nitric acid (65%, G.R.), Hydrochloric acid (37%, G.R.) from Beijing Chemical Works were used during the experiment process. The quartz sand was digested in aqua regia for 2 hours, and rinsed with ultrapure water to neutral, dried and stored in the desiccators.

The 1000 mg L^{-1} single element stock reference solutions of Cu, Mn, Zn, Pb, Cr, Cd, Ni and Co (NCS, China Iron & Steel Research Institute Group, China) were used to prepare working analytical solutions by serial dilution in nitric acid aqueous solution (8%, w/w) for ICP-AES. The Certified Reference Material GBW07401-GSS-1 Soil (NRCCRM, Institute of Geophysical and Geochemical Exploration, China) and GBW 08303 Soil (NRCCRM, Beijing Municipal Environmental Monitoring Center, China) supplied by the National Research Center for Certified Reference Material (NRCCRM) were used for the method validation in Section 3.3. The former was dark brown earth from Xilin lead-zinc ore district in Heilongjiang Province of China, and the latter was polluted agricultural soil. All glassware and plastic materials used were soaked in nitric acid aqueous solution (10%, w/w) for 48 hours and rinsed with ultrapure water.

2.3. Sample collection and preparation

Natural soil sample 1, 2 and 3 were collected from different places in Changchun City, and sample 4, 5 and 6 were collected from different agricultural fields in Jilin City. The natural soil samples (1-2 kg) were air-dried in fume cupboards and ground to break down aggregates in a porcelain mortar. Then each kind of the samples was divided into four parts, and sieved with nylon of different sieves to particle size of 149 μm, 75 μm, 53 μm and 45 μm, respectively. The sieved soils obtained were stored in polyethylene bottles in desiccators at room temperature. The physical and chemical properties of the natural soil samples were shown in Table 2.

2.4. Procedure

2.4.1 MTDMAL procedure

Firstly, 1.000 g soil sample was accurately weighed and mixed with 3 g quartz sand (used as dispersant agent). The mixture was transferred to the leaching vessel fitted with the sieve plate containing a layer of 2g quartz sand, and then the top of the leaching vessel was fitted with another sieve plate. Four samples and one blank were loaded with the same method and arranged systematically in the microwave oven, and connected with the leachant container and the ports of the vacuum SPE manifold by T_1 and T_2 (Fig. 1).

Subsequently, the vacuum pump was activated and leachant passed through the leaching vessel. When the leachant was pumped into the leaching vessel thoroughly, microwave irradiation was started with the power of 375 W. When the collection volume was 20 mL, the microwave irradiation was stopped and 10 mL of ultrapure water was pumped into the polyethylene tubes for rinse. The collected solution was diluted to 50 mL, and centrifuged before ICP-AES analysis.

2.4.2 Conventional digestion method

The conventional digestion procedure was based on standard method of China (NY/T 1613-2008). Accurately weighed 1.000g soil sample and 10 mL of concentrated nitric acid were transferred into triangular flask contained with a glass bead. The flask was heated to keep a slightly boiling state on hot plate until 7 mL left. Then 20 mL of concentrated hydrochloric acid was added to the flask. It was heated to keep a slightly boiling state for 2 h, and then the mixture was volatilized to wet salt state and 10 mL of ultrapure water was added. The mixture was fully transferred into a centrifuge tube and centrifuged for 2 min, and then diluted to 50 mL. The solution was finally analyzed by ICP-AES.

2.5. Leaching efficiencies

The conventional digestion procedure was regarded as reference to evaluate the leaching efficiencies of the proposed MTDMAL method. The leaching efficiencies were calculated using the following method:

$$\text{Leaching efficiency}(\%) = \frac{C_{\text{MTDMAL}}}{C_{\text{Reference}}} \times 100\%$$

C_{MTDMAL}: metal content in soil obtained with MTDMAL method.

$C_{\text{Reference}}$: certified value of metal content in soil or those obtained with conventional digestion procedure.

All the procedures were performed at least three times and the mean values were reported.

3. Results and discussion

3.1 Optimization of the dynamic microwave system

3.1.1 Microwave radiation power

Microwave radiation accelerates the leaching process and the experimental results are as expected. It is found that microwave power has distinct effect on the leaching efficiencies of the heavy metals and larger microwave power is helpful to improve the leaching efficiencies. The effect of microwave power of 600 W and 750 W could not be evaluated, since the leachant cannot go through the sample vessel due to a fierce ebullition over the vessel. The leaching efficiencies of the heavy metals were too low at power of 75 W (not shown). The results indicate that the leaching efficiencies of the heavy metals with 375 W are better than 225W (Fig. 2A). Thus, the microwave power of 375 W was selected in the subsequent experiment.

3.1.2 Kinds and concentrations of leachants

The leachant should have enough oxidability and corrosivity to destroy soil lattice and release metal ions to the solution. Firstly, we investigated the effect of nitric acid aqueous solution, aqua regia aqueous solution and athwart aqua fortis aqueous solution as leachant. The results (Fig. 2B) demonstrated that the best leaching efficiencies of the heavy metals were achieved with nitric acid aqueous solution.

Furthermore, the effect of the concentration of nitric acid aqueous solution on the leaching efficiencies of the heavy metals was investigated. The experiments were performed with 20 mL of nitric acid aqueous solution (15–35%, w/w) and the results are shown in Fig. 2C. The leaching efficiencies of the heavy metals increase with the nitric acid concentration, and remain relatively constant when the concentration is above 20%. Therefore, nitric acid aqueous solution (20%, w/w) was chosen as leachant in the following experiment.

3.1.3 Particle size of soil samples

We investigated the influence of particle size of soil samples on the leaching efficiencies of the heavy metals. The soil samples with particle size of 149 μm, 75 μm, 53μm and 45μm were tested. The results (Fig. 2D) show that the higher leaching efficiencies followed with smaller particle size of soil samples, while the leachant couldn't go through swimmingly the soil samples with the particle size of 53μm and 45μm. In view of this regard, the soil samples with particle size of 75 μm were selected in the experiment.

3.1.4 Collection volume

Under the certain flow rate, the leaching time depends on the collection volume, and we investigated the effect of the volume on the leaching efficiencies from 10 mL to 30 mL (Fig. 2E). The satisfactory results were obtained with collection volume of 20 mL and the leaching efficiencies remain relatively constant when the collection volume is above 20 mL. In consideration of less consumption of reagent and time, collection volume of 20 mL was finally selected, which can be completed in about 15 min.

3.1.5 Soak time

The leaching efficiencies of Cu, Mn, Zn and Pb were comparable with the conventional method under the optimized condition, while the leaching efficiencies of Cr, Cd, Ni and Co were relatively lower. In consideration of the shorter contact time between the leaching reagent and the sample, a soak process using 1 mL of leachant before MTDAML procedure was carried out with different soak time 0 h, 12 h, 24 h and 48 h, respectively.

When the soak progress was appended, the leaching effect of Cr, Cd, Ni, Co has certain extent enhancement by 10–50% in the studied samples. Under the soak time of 48 h, it significantly improved the leaching efficiencies of Cr, Cd, Ni, Co from 43.9%, 38.8%, 64.9%, 79.7% to 73.1%, 91.4%, 85.9%, 87.4%, respectively (Fig. 2F). As for Cu, Mn, Zn and Pb, the leaching efficiencies had no significant increase with the soak progress. It indicated that the additional soak process supplied enough time to destroy the soil lattice and facilitate the leaching of Cr, Cd, Ni and Co.

3.2 Performance of the method

The limit of detection (LOD) and limit of quantitation (LOQ) were three times and ten times the standard deviation (n=11) of the blank, respectively. The LODs of Cu, Mn, Zn and Pb ranged from 0.0002 to 0.006 μg ml^{-1}, and the LOQs ranged from 0.0007 to 0.02 μg ml^{-1} (Table 3), which was comparable with those in literature[10]. The linear correlation coefficients were higher than 0.99 for all the heavy metals in regression analysis.

Precisions were evaluated by measuring intra- and inter-day relative standard deviations (RSDs). The intra-day precision of the method was performed by analyzing six identical samples in one day, and the inter-day precision was performed by analyzing the samples once a day over six consecutive days. The RSDs of intra- and inter-day were in the range of 1.7–6.3% and 5.0–6.9% for Cu, Mn, Zn and Pb, respectively (Table 4), and comparable with those in literature.[10,21] The inadequate dissolution resulted in the higher RSDs of Cr, Cd, Ni, Co under the proposed method. The proposed method has two advantages: the less time consumption and simplification of sample preparation versus MAD (15 min versus 1-2 h)[16-19], the higher throughput of sample versus microwave assisted leaching technique (five versus two)[20-22].

3.3 Validation and application of the proposed method

In order to evaluate the compatibility and accuracy of the proposed method, we analyzed the heavy metals in Certified Material GBW 07401-GSS-1 Soil and GBW 08303 Soil with the soak progress. The contents of the heavy metals in the certified soils obtained with the proposed method were compared with the certified values (Table 5).

The natural soil samples were employed to further validate the applicability of the method with the soak progress, and the results were compared with those of conventional digestion method. Obviously, the MTDMAL method was effective to leach Cu, Mn, Zn and Pb with leaching efficiencies above 95% for the studied samples, as shown in Table 6.

The leaching efficiencies of Pb in the studied soil samples were among

109.5%-132.1%, perhaps because the closed MTDMAL system avoided the volatilization loss of Pb caused by acid-evaporation process in the conventional method. It can be estimated that the system may be propitious to leach volatile elements from soil, such as As, Se and Hg. The leaching efficiencies of Zn in the natural soil samples were above 100%, and it agreed well with the results of the literature that microwave could improve the leaching efficiency of Zn[27].

The leaching effciencies of Cr, Cd, Ni and Co were still lower than the other metals' with an additional soak progress. The leaching efficiencies of Cd in Certified Material GBW 07401-GSS-1 and GBW 08303 were higher than that in the natural soil samples, perhaps it's due to the difference between the Certified Material and natural soil samples. We speculate that the leaching efficiency is in connection with the different speciation distributions of heavy metals in soils. The study about metal speciation in soil and sediment indicated that Cr, Cd, Co and Ni mainly existed in residue[28-30], Cu, Mn, Zn and Pb mainly existed in acid extractable phase[31-34], which means the latter is easier to be dissolved than the former[35]. In addition, the relatively lower leaching efficiencies of Cr, Ni are perhaps owing to the absence of HF in the leachant, which is insufficient to destroy the soil lattice as shown in the literature[27]. All of the above reasons result in the lower leaching effciencies of Cr, Cd, Ni, Co compared with Cu, Mn, Zn and Pb in the studied soil samples.

4. Conclusion

In this study, a multi-throughput dynamic microwave-assisted leaching method was first used for the leaching of heavy metals in soils, followed by ICP-AES determination. A rapid and convenient determination of Cu, Mn, Zn and Pb in soil has been realized under the optimized condition. The leaching efficiencies of Cr, Cd, Ni and Co have certain enhancement with an additional soak progress. The whole leaching process was performed in a closed system with nitric acid aqueous solution used as leachant, thereby reducing risks of environmental pollution and volatilization loss of Pb. The leachates were directly analyzed after centrifugation and dilution, thereby simplify manual handling and decrease preparation time. In conclusion, the main benefits of the proposed method are eco-friendly, less consumption of acid, simplification of sample preparation in a short period. The method may have a broad prospect for leaching volatile elements from soil such as As, Se and Hg if combined with compatible detecting instrumentation.

Acknowledgments

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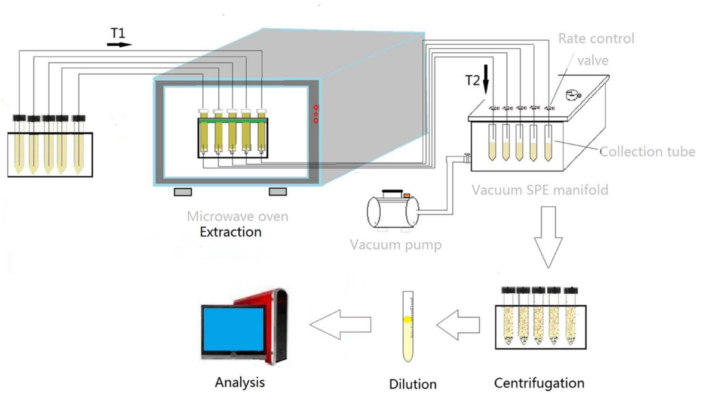
359 **Figure legends**

360 **Fig. 1** Schematic diagram of the MTDMAL system.

361 **Fig. 2** Effect of the different parameters on the leaching efficiencies of the heavy metals (n = 3), (A) Microwave power; (B) Kinds of leachant; (C) Nitric acid concentration; (D) Soil particle size; (E) Collection volume; (F) Soak time.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T2
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valve
Collection tube
Vacuum SPE manifold
Microwave oven
Extraction
Vacuum pump
Analysis
Dilution
Centrifugation

Fig. 1

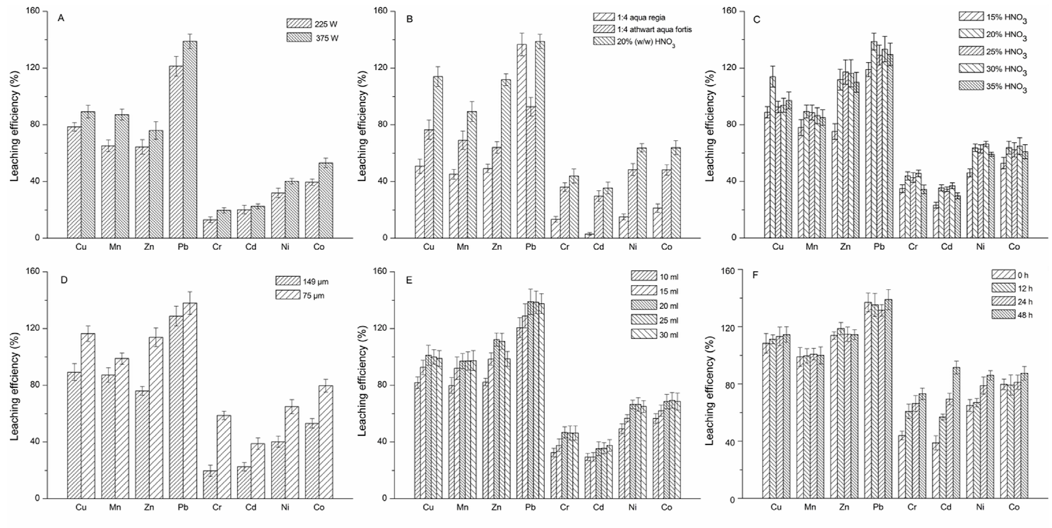

A
225 W
375 W
B
1:4 aqua regia
1:4 athwart aqua fortis
20% (w/w) HNO3
C
15% HNO3
20% HNO3
25% HNO3
30% HNO3
35% HNO3
D
149 μm
75 μm
E
10 ml
15 ml
20 ml
25 ml
30 ml
F
0 h
12 h
24 h
48 h
Leaching efficiency (%)
Cu Mn Zn Pb Cr Cd Ni Co

Fig. 2

Table 1 Instrumental parameters for Cu, Mn, Zn, Pb, Cr, Cd, Ni and Co determination by ICP-AES

Parameter	
RF power (W)	1300
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	0.5
Nebulizer gas flow rate (L min^{-1})	0.80
Pump flow rate (mL min^{-1})	1.5
Speed (RPM)	29.43
Element	Wavelength (nm)
Cu	324.752
Mn	257.610
Zn	213.857
Pb	220.353
Cr	267.716
Cd	214.440
Ni	231.604
Co	228.616

Table 2 The physicochemical properties of the natural soil samples

Soils	pH	Organic (%)	Carbonates (%)	Cation-exchange capacity (cmol kg^{-1})	Sand (%) (2>d>0.02)[a]	Silt (%) (0.02>d>0.002)[a]	Clay (%) (d<0.002)[a]
1	6.9	4.5	4.2	35.6	62.1	27.2	10.7
2	7.2	3.8	2.0	53.9	50.4	37.8	11.8
3	6.7	0.2	0.1	45.3	24.5	29.4	46.1
4	6.7	1.7	1.1	43.4	29.4	34.5	36.1
5	6.6	1.6	1.9	48.6	26.2	28.6	45.2
6	6.7	2.4	1.3	51.2	45.2	28.6	26.2

[a] d: particle diameter (mm).

Table 3 Analytical characteristic of the ICP-AES method

Element	Linearity range ($\mu g\ mL^{-1}$)	Calibration equation	Correlation coefficient (r^2)	LOD ($\mu g\ mL^{-1}$)	LOQ ($\mu g\ mL^{-1}$)
Cu	0.003~100	Y = 32739x + 125	0.9997	0.0007	0.003
Mn	0.007~1000	Y = 59033x – 2052	0.9999	0.002	0.007
Zn	0.001~500	Y = 9512.2x + 148	0.9998	0.0004	0.001
Pb	0.02~250	Y = 419.2x + 0.1	0.9996	0.006	0.02
Cr	0.007~100	Y = 9892.2x – 38.5	0.9991	0.002	0.007
Cd	0.0007~5	Y = 80180x – 50.3	0.9991	0.0002	0.0007
Ni	0.01~50	Y = 3158.4x – 8.4	0.9998	0.003	0.01
Co	0.007~50	Y = 1960.4x + 3.3	0.9996	0.002	0.007

Table 4 Intra- and inter-day relative standard deviations (RSDs) of the proposed method (n = 6)

Element	intra-day		inter-day	
	Content/mg kg^{-1}	RSD/%	Content/mg kg^{-1}	RSD/%
Cu	20.5	5.4	20.5	5.7
Mn	1671.6	6.3	1708.3	6.3
Zn	644.6	1.7	649.1	5.0
Pb	108.8	2.7	110.3	6.9
Cr	39.6	6.5	38.3	9.3
Cd	5.7	4.9	5.8	8.6
Ni	12.7	8.5	12.1	8.9
Co	8.9	4.0	9.1	7.1

Table 5 Determination of heavy metals in certified soils.

	GBW07401-GSS-1			GBW08303		
Element	Certified value	Found value	Leaching efficiencies/%	Certified value	Found value	Leaching efficiencies/%
Cu	21±2	20.5±0.3	97.6	120±6	116±5	96.7
Mn	1760±63	1692±76	96.1	519±18	510±15	98.3
Zn	680±25	648±35	95.2	260±11	253±12	97.3
Pb	98±6	110±4	111.8	73±2	81±2	111.9
Cr	62±4	39±2	62.2	112±6	89±5	79.4
Cd	4.3±0.4	5.3±0.4	122.6	1.2±0.1	1.25±0.08	104.2
Ni	20.4±1.8	12.3±0.4	60.1	40±2	31.0±1.8	78.1
Co	14.2±1.0	9.3±0.4	65.5	13.0±0.6	9.0±0.5	69.2

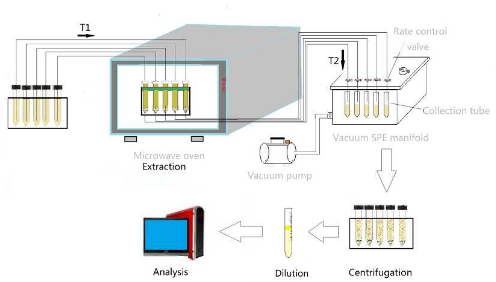
All values reported as mean (n = 3) ± SD (mg kg^{-1} dried basis).

392 **Table 6** Application of the proposed method

Element	Sample 1 Reference value[b]	Sample 1 Found value[a]	Sample 1 Leaching efficiencies/%	Sample 2 Reference value[b]	Sample 2 Found value[a]	Sample 2 Leaching efficiencies/%	Sample 3 Reference value[b]	Sample 3 Found value[a]	Sample 3 Leaching efficiencies/%
Cu	62±3	64±3	104.3	19±5	21±5	112.1	20±3	19±3	95.9
Mn	540±5	540±21	99.9	511±19	520±23	101.8	517±18	503±15	97.2
Zn	263±3	300±14	114.4	85±2	95±2	112.2	69±1	74±1	107.8
Pb	83±5	104±6	125.6	16.1±1.6	21±2	132.1	10.6±1.1	12±1	112.7
Cr	46.8±1.0	34.2±1.2	73.1	25.5±0.1	17.0±0.3	66.7	33±1	22±1	66.7
Cd	1.7±0.1	1.4±0.1	82.3	1.7±0.8	1.5±0.7	85.3	1.8±0.2	1.2±0.1	70.3
Ni	20.8±0.6	17.9±1.1	85.9	20.3±0.8	16.5±1.1	81.5	26.2±0.5	18.4±0.3	70.1
Co	13.3±0.2	11.6±0.4	87.4	10.8±0.4	9.2±0.8	85.5	11.4±0.2	7.7±0.2	67.8
Element	Sample 4 Reference value[b]	Sample 4 Found value[a]	Sample 4 Leaching efficiencies/%	Sample 5 Reference value[b]	Sample 5 Found value[a]	Sample 5 Leaching efficiencies/%	Sample 6 Reference value[b]	Sample 6 Found value[a]	Sample 6 Leaching efficiencies/%
Cu	12.2±3.2	11.9±3.0	97.4	9.5±1.4	9.7±1.6	102.5	16±3	15.7±2.6	96.5
Mn	675±21	664±23	98.4	623±25	601±26	96.6	615±22	606±23	98.6
Zn	87.5±1.8	102±2	116.3	63.2±2.8	65.4±1.8	103.6	81.2±1.6	82.5±1.8	101.6
Pb	14.6±1.3	16.2±1.4	110.9	10.3±1.1	12.2±0.9	118.2	13±1	14.2±0.9	109.5
Cr	23.8±1.3	16.0±1.4	66.8	57±2	40.1±1.5	70.3	29.4±1.0	18±1	61
Cd	1.9±0.2	1.7±0.2	88.2	1.0±0.1	0.7±0.1	68.6	1.6±0.3	1.2±0.2	72.6
Ni	15.8±0.3	11.6±0.2	73.1	26±2	17.2±0.9	76.7	19.1±0.6	14.6±0.4	76.7
Co	10.8±0.3	7.5±0.1	69.8	56±3	48±2	86.8	11.6±0.3	7.7±0.3	66.8

393 All values reported as mean (n = 3) ± SD (mg kg^{-1} dried basis).

[a]Obtained with MTDMAL method, [b]Obtained with conventional digestion method (NY/T 1613–2008 method).



The approach combines the advantages of microwave and dynamic extraction technique, and up to five soil samples can be treated at the same time within 15 min. The leachates were centrifugated and diluted before ICP-AES determination, instead of the cumbersome step of acid-evaporation, transfer, and filtration in the conventional digestion procedure.

Figure legends

Fig. 1 Schematic diagram of the MTDMAL system.

Fig. 2 Effect of the different parameters on the leaching efficiencies of the heavy metals (n = 3), (A) Microwave power; (B) Kinds of leachant; (C) Nitric acid concentration; (D) Soil particle size; (E) Collection volume; (F) Soak time.

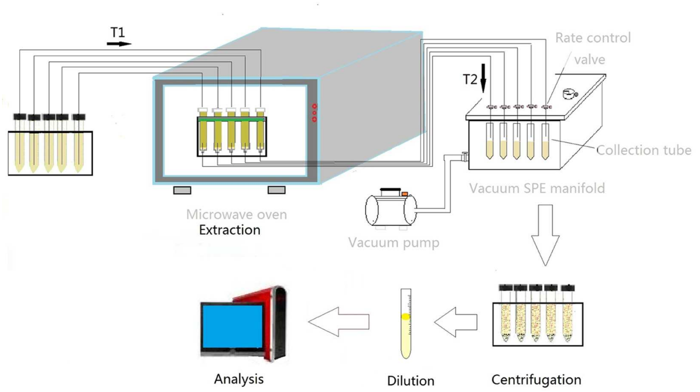

T1
T2
Rate control
valve
Collection tube
Vacuum SPE manifold
Microwave oven
Extraction
Vacuum pump
Analysis
Dilution
Centrifugation

Fig. 1

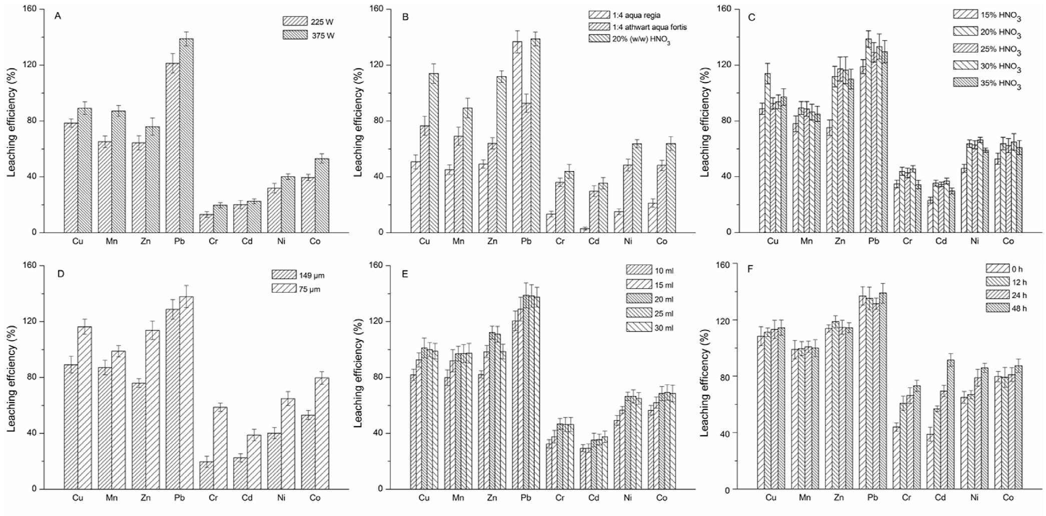

A
225 W
375 W
B
1:4 aqua regia
1:4 athwart aqua fortis
20% (w/w) HNO3
C
15% HNO3
20% HNO3
25% HNO3
30% HNO3
35% HNO3
D
149 μm
75 μm
E
10 ml
15 ml
20 ml
25 ml
30 ml
F
0 h
12 h
24 h
48 h
Leaching efficiency (%)
0
40
80
120
160
Cu
Mn
Zn
Pb
Cr
Cd
Ni
Co

Fig. 2