Application of ultrasonic to speciation analysis of heavy metals in soil

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Abstract: In order to reduce the operation time and improve the extraction efficiency, ultrasonic energy by means of ultrasonic bath was used to the modified Tessier sequential extraction for speciation analysis of heavy metals in soil. Extractable contents of Cu, Fe, Mn, Ni, Pb and Zn were measured by atomic absorption spectroscopy(AAS). The merit of the ultrasonic extraction(UE) applied to the modified Tessier method is not only that the operation time for the first 4 fractions was reduced from ca. 18 h to 8 h, comparing with conventional extraction(CE), but also the extraction efficiency was higher. The results for both of UE and CE were consistent. The extractable Cu, Ni and Zn in the sample No. 1 were mainly associated with the third fraction(Fe-Mn oxides fraction), and fourth fraction(organic matter fraction) in the sample No. 2. The extractable Fe and Mn were all mainly associated with the third fraction, and Pb the fourth fraction in both of the samples. The effects of concentration of hydroxylamine chloride on the capability for the extraction of studied metals were also studied.

Keywords: speciation analysis; heavy metal; sequential extraction; ultrasonic extraction; soil; atomic absorption spectrometry

Introduction

The knowledge of the total concentration of heavy metals in soil is useful, and, in many situations is all required. In many fields, however, it is increasingly being recognized that the chemical form of the heavy metals is more important and using modern analytical tools it is often available to measure not only how much of heavy metals is existed but what speciation it has. Heavy metals are present in many forms, and speciation studies of heavy metals play a significantly important role in many aspects of soil, sediment and pollution science. They provide an aid to understanding the mechanisms of transport, mobilization, trapping and transformation of trace elements in soil, sediment and sludge.

Single extract designed to isolate a particular species is seldom sufficiently specific for not only assessment of bioavailability but also isolation and determination of elements bound or associated with different soil fractions or phases, and will in general extract other species to some extent. An improvement in the specificity of extraction could be achieved by combining single extracts into a sequential extraction scheme in which the residue from the preceding extraction is extracted by the next extract in the sequence. Sequential extraction procedures do, however, offer the major advantage that they simulate to a certain extent various environmental conditions to which the soil or sediment may be subjected; deductions can then be made about the trace metal levels likely to be observed under these conditions in the environment (Tessier, 1979). There are many different sequential extraction schemes. Procedures designed for sediments include the pioneering work of Presley et al. (Presley, 1972) and of Tessier et al. (Tessier, 1979). The latter has been one of the most popular schemes, and the

most modified sequential extraction schemes(Towner, 1985; Meguellati, 1983) are based on this scheme which was designed for bringing different fractions of metal pollutants existed in different aquatic sediment phases into solution. The phases are operationally defined as exchangeable(1 mol/L $MgCl_2$), carbonate bound(1 mol/L NaOAc adjusted to pH 5 with HOAc), bound to Fe-Mn oxides(0.04 mol/L NH_2OH ·HCl in 25% v/v HOAc), bound to organic matter(H_2O_2 adjusted to pH 2 with HNO_3) and residual (HF-$HClO_4$ digestion) (Tessier, 1979).

Although the sequential extraction scheme proposed by Tessier et al. is widely applied, the operation time for the extraction is long and tedious. The operation time for the first 4 fractions by using the Tessier method is about 18 h, and the modified Tessier methods were about the same with it. The means of ultrasonic energy or microwave is used to accelerate the extraction of component in sample and reduces the operation time. Perez-Cid et al. applied ultrasonic energy by a means of probe to accelerate the sequential extraction methods of Tessier. No significant differences were found for Cu, Cr, Ni, Pb and Zn in the two first fractions, however, in the third and fourth extracts the extraction capability of the conventional and ultrasonic methods differed significantly(Perez-Cid, 1999).

The purpose of this study is to develop a method for speciation analysis of heavy metals in soil, sediment or sludge by ultrasonic energy using a means of ultrasonic cleaning bath in order to shorten the extraction time and improve the extraction efficiency. The speciation for heavy metals of Cu, Fe, Mn, Ni, Pb and Zn in the soil samples collected from a steel factory was studied, using a modified Tessier's 5-step scheme. The effect of concentration of hydroxylamine hydrochloride on the extraction of the studied metals was also

studied.

1 Materials and methods

1.1 Apparatus

A Model 3510 AAS (Agilent Technology Company, Shanghai, China) was used to determine the metal concentration in the extracts. Hollow cathode lamps of Cu, Fe, Mn, Ni, Pb and Zn were used as the radiation source, and their resonance lines employed were 324.8, 248.3, 279.2, 232.1, 217.0 and 279.2 nm, respectively. The lamp intensity and slit width used for all experiments were 2 mA and 0.2 nm, respectively according to the manufacturer's recommendations. The air-acetylene flow rate was 5—1 dm^3/min (5 dm^3/min for air and 1 dm^3/min for acetylene). A model RS-18A ultrasonic cleaning bath with heating and timer (180 W power and 35 kHz frequency, Rongshun Instruments Company of Scientific and Technology, Ningbo, Zhejiang, China) was used for supersonic extraction.

1.2 Reagents

All reagents used were of analytical reagent grade. The water used was obtained by distilling deionized water two times. Hydroxylamine hydrochloride in 25% (v/v) acetic acid and aqua regia were prepared prior to use.

1.3 Sampling and pre-treatment

Soil samples were collected at two sites of a steel company located in the suburb of Suzhou City, China, named No.1 and 2. In the laboratory the samples were dried at room temperature, then they were ground in an agate mortar and fractionated using 100, 160 and 200 nylon mesh sieves, successively. The sieved samples were homogenized well and stored in polyethylene bottles. The determined value by AAS was the average figure of triplicate measurements.

1.4 Selection of extraction mode

Three grams of the 200 mesh soil sample No.1 were extracted for 5 h with 15 ml of 0.5 mol/L NaOAc adjusted to pH 5.0 with HOAc by the UE and the CE, respectively, and the concentrations of Mn and Fe in the extracts were determined.

1.5 Effect of time and temperature on efficiency of UE

Three grams of the 200 mesh soil sample No.1 were extracted with 15 ml of 0.5 mol/L NaOAc adjusted to pH 5.0 with HOAc at room temperature for 10, 20, 30, 40, 60, 90, 180 min, respectively to optimize the extraction time of the UE. The same weight of the sample was extracted for 90 min at temperatures of 30, 40, 50 and 60℃, respectively to see the effect of temperature on the UE.

1.6 Sequential extraction procedure by two extraction modes

The Tessier sequential extraction method (Tessier, 1979) was slightly modified and the steps are as follows: 3 g of the 200 mesh soil samples were placed in a 50 ml polyethylene centrifuge tube with cover. The reagents and operating conditions employed are summarized in Table 1. The extractions of the first 4 steps were carried out in the tube and then centrifuged at 4000 r/min for about 10 min to shorten separation time and minimize possible losses of the sample in the successive steps of the sequential extraction. The supernatant liquid was transferred into polyethylene bottles and stored at 3—4℃ in a refrigerator until analysis. The remaining solid residue was washed with 10 ml of the water and the washings were discarded after centrifuge.

Table 1   Operation conditions used in the modified Tessier sequential extraction scheme

Step	Fraction	Reagent	Experimental conditions	
			Conventional extraction[a]	Ultrasonic extraction[b]
1	Exchangeable	25 ml of 0.5 mol/L $MgCl_2$ (pH 7)	1 h at room temperature	1.5 h at 50℃
2	Related to carbonates	25 ml of 0.5 mol/L NaOAc-HOAc (pH 5)	5 h at room temperature	1.5 h at 50℃
3	Related to Fe-Mn oxides	25 ml 0.04 mol/L $NH_2OH \cdot HCl$ in 25% (v/v) HOAc	6 h at 85℃ in water bath	1.5 h at 85℃
4	Related to organic matter	4.5 ml of 0.02 mol HNO_3 and 7.2 ml of H_2O_2 (pH 2 with HNO_3)	2 h at 85℃ in water bath	1.5 h at 85℃
		Add 4.5 ml of H_2O_2 (pH 2 with HNO_3)	3 h at 85℃ in water bath	1.5 h at 85℃
		Add 8.8 ml of 3.2 mol NH_4OAc in 20% (v/v) HNO_3	30 min at room temperature	30 min at room temperature
5	Residual	15 ml of aqua regia	2 h reflux heating	2 h reflux heating

Notes: [a] The extraction of heavy metals in the soils for the first two fractions was carried out by using the mechanic shaker; [b] The extraction of heavy metals in the soils for the first four fractions was carried out by using the ultrasonic cleaning bath

1.7 Concentration of $NH_2OH \cdot HCl$ on capability of extraction of heavy metals

Three grams of the 200 mesh soil sample No.1 were placed in a 50 ml polyethylene centrifuge tube with cover and extracted for 1.5 h by 25 ml of 0.04, 0.1, 0.2, 0.3 mol/L $NH_2OH \cdot HCl$ in 25% HOAc by the UE, respectively.

2 Results and discussion

2.1 Particle size and homogeneity of sample

The samples sieved through 100, 160 and 200 mesh were extracted with 0.02 mol/L EDTA in 0.5 mol/L HOAc and in general, the sample particle size was smaller, the extraction efficiency and the homogeneity were higher. The RSDs for the determination of Mn and Pb in the samples sieved by 200 mesh were between 4.8%—6.3% and 0.8%—1.2%, and it is considered that the particle size and homogeneity of the sample were good enough for the speciation analysis.

Table 2   Results for species of heavy metals in soil by means of both ultrasonic and conventional sequential extractions

		Mean and standard deviation[a]							
		Soil No. 1				Soil No. 2			
Metal	Fraction	UE, μg/g	CE, μg/g	Aqua regia, μg/g	Extraction efficiency, %[b]	UE, μg/g	CE, μg/g	Aqua regia, μg/g	Extraction efficiency, %
Cu	1. Exchangeable	0.54 ± 0.08	0.52 ± 0.16		104	0.58 ± 0.09	0.35 ± 0.03		166
	2. Related to carbonate	0.99 ± 0.12	0.81 ± 0.03		122	0.93 ± 0.07	0.42 ± 0.01		221
	3. Related to Fe-Mn oxide	3.69 ± 0.32	3.96 ± 0.28			5.31 ± 0.1	7.76 ± 1.0		
	4. Related to organic matter	1.82 ± 0.88	2.34 ± 0.48			21.5 ± 1.1	21.1 ± 0.4		
	5. Residual	17.8 ± 2.9	13.7 ± 1.8			24.9 ± 1.0	22.9 ± 1.8		
	Σ (1 + 2 + 3 + 4 + 5)	24.8 ± 1.1	21.3 ± 1.0			53.2 ± 3.2	52.6 ± 2.9		
	M_T^c			25.1 ± 0.19				50.5 ± 1.3	
Fe	1. Exchangeable	5.95 ± 0.26	5.33 ± 0.25		739	5.96 ± 0.18	3.39 ± 0.10		167
	2. Related to carbonate	0.83 ± 0.05	0.67 ± 0.05		1120	5.48 ± 0.17	2.99 ± 0.09		111
	3. Related to Fe-Mn oxide	2120 ± 40	2020 ± 40			4440 ± 89	4370 ± 85		
	4. Related to organic matter	296 ± 12	315 ± 15			893 ± 18	815 ± 16		
	5. Residual	1530 ± 10	1580 ± 20			38100 ± 760	38800 ± 780		
	Σ (1 + 2 + 3 + 4 + 5)	3940 ± 40	3920 ± 60			43400 ± 1300	44000 ± 1320		
	M_T^c			3980 ± 60				46100 ± 1380	
Mn	1. Exchangeable	10.5 ± 0.77	4.10 ± 0.32		256	54.4 ± 4.9	21.6 ± 0.2		252
	2. Related to carbonate	21.1 ± 0.26	16.3 ± 0.59		129	74.4 ± 5.8	25.7 ± 2.5		289
	3. Related to Fe-Mn oxide	426 ± 11	403 ± 20			143 ± 14	212 ± 26		
	4. Related to organic matter	27.5 ± 0.3	27.8 ± 1.1			57.2 ± 3.7	62.1 ± 7.1		
	5. Residual	47.9 ± 2.2	46.4 ± 2.0			90.7 ± 5.7	76.7 ± 9.2		
	Σ (1 + 2 + 3 + 4 + 5)	533 ± 14	498 ± 22			420 ± 32	398 ± 35		
	M_T^c			625 ± 20.9				380 ± 2.4	
Ni	1. Exchangeable	2.44 ± 0.19	0.33 ± 0.06		112	0.60 ± 0.09	0.36 ± 0.07		176
	2. Related to carbonate	6.60 ± 0.68	0.59 ± 0.05		124	1.76 ± 0.12	1.58 ± 0.03		183
	3. Related to Fe-Mn oxide	9.18 ± 0.46	11.1 ± 0.84			2.11 ± 0.15	3.18 ± 0.32		
	4. Related to organic matter	8.00 ± 0.30	7.91 ± 0.52			3.95 ± 0.20	4.01 ± 0.03		
	5. Residual	40.6 ± 1.1	43.3 ± 1.5			19.7 ± 0.3	17.2 ± 0.5		
	Σ (1 + 2 + 3 + 4 + 5)	66.8 ± 3.1	63.2 ± 2.9			28.1 ± 0.4	26.4 ± 0.5		
	M_T^c			79.9 ± 1.0				29.6 ± 0.5	
Pb	1. Exchangeable	1.01 ± 0.08	0.68 ± 0.06		149	0.78 ± 0.06	0.35 ± 0.02		223
	2. Related to carbonate	0.45 ± 0.04	0.43 ± 0.04		105	2.77 ± 0.10	1.67 ± 0.09		166
	3. Related to Fe-Mn oxide	11.9 ± 0.5	11.8 ± 0.6			16.7 ± 0.6	20.3 ± 0.8		
	4. Related to organic matter	12.3 ± 0.6	12.0 ± 0.4			21.3 ± 0.9	18.2 ± 0.7		
	5. Residual	5.50 ± 0.25	4.86 ± 0.36			19.8 ± 0.8	16.4 ± 0.6		
	Σ (1 + 2 + 3 + 4 + 5)	31.2 ± 1.1	29.8 ± 1.2			61.4 ± 2.5	56.9 ± 2.3		
	M_T^c			30.2 ± 0.6				61.0 ± 1.4	
Zn	1. Exchangeable	0.73 ± 0.05	0.69 ± 0.04		106	0.61 ± 0.03	0.33 ± 0.01		185
	2. Related to carbonate	3.88 ± 0.08	3.29 ± 0.07		118	15.9 ± 0.5	14.5 ± 0.4		110
	3. Related to Fe-Mn oxide	25.1 ± 0.5	23.8 ± 0.5			3.95 ± 0.1	4.22 ± 0.2		
	4. Related to organic matter	15.1 ± 0.3	15.9 ± 0.3			34.5 ± 0.6	33.2 ± 0.7		
	5. Residual	67.5 ± 1.4	63.6 ± 0.06			72.7 ± 1.2	64.4 ± 1.0		
	Σ (1 + 2 + 3 + 4 + 5)	112 ± 3	107 ± 3			128 ± 2.6	117 ± 2.3		
	M_T^c			121 ± 4				136 ± 2.8	

Notes: a. Mean and standard deviation are calculated on three replicate determinations; b. value of extraction efficiency is calculated on the ratio of fractional content of heavy metal extracted by using the UE to that of the CE; c. M_T represents the total metal concentration determined directly by digestion using aqua regia

2.2   Comparison of extraction efficiency between UE and CE

The required time for the sequential extraction in the speciation analysis of heavy metals is long and tedious since the extraction efficiency of the CE is not high. The advantages of UE are that it makes use of the cavitation of supersonic wave in liquid to extract determined components from solid samples or solid substrates into extract. When irradiated by supersonic wave, the liquid of extract can produce unstable minute vacuum bubbles. Under the action of acoustic filed, these bubbles shrink and expand, the liquid particles come into violet contact with each other thousands of times a second. As a result, a very powerful energy is generated. This impact force is as strong as 0.5— 20 ton/cm^2 and becomes an accelerator of the liquid with force exceeding 10 kg, which enables the extraction of determined compounds from the solid samples into the liquid of extract.

The average contents of Mn and Fe in the soil sample No.1 by the UE for 0.5 h at the room temperature were 15.5 and 1.21 μg/g, and by the CE for 5 h were 14.1 and 1.01

μg/g. It was that not only the operation time was only tenth of that by the CE extraction mode but the contents of Mn and Fe extracted from the sample by the UE were higher than that obtained by the CE. Obviously, it can be concluded that the efficiency for extraction of heavy metal by UE was higher than that obtained by the CE. This result was consistent with that of Christine et al., who reported that an ultrasonic cleaning bath and an ultrasonic probe have been used to develop rapid versions of the three-stage Community Bureau of Reference sequential extraction procedure (Davidson, 2001). Thereafter, the UE by means of the ultrasonic cleaning bath was applied to the sequential extraction for the speciation analysis of heavy metals from the soils in the further study.

2.3   Effects of extraction time and temperature on UE efficiency

To optimize the UE of the species of heavy metals from soil, the extraction time and temperature were tested, respectively. The effect of extraction time on the UE efficiency is shown in Fig.1. It is shown that the obtained contents of Mn and Fe in the soil sample No.1 were enhanced when the extraction time increased from 10 to 90 min. When

the extraction time was 120 min, the results for the Mn and Fe contents in the sample were almost the same with those of 90 min. Therefore, 90 min was selected for the UE in this work.
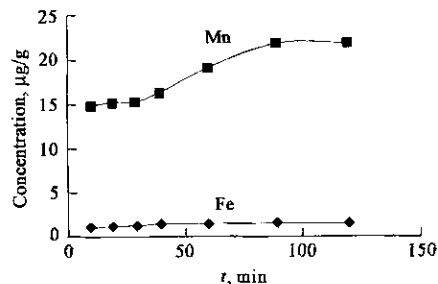

Fig.1 Effect of time on UE efficiency

The temperature of 30, 40, 50 and 60℃ in the ultrasonic cleaning bath were tested to optimize the extraction efficiency for the heavy metals from soil. The result is shown in Fig. 2 and it is seen that the values of Mn and Fe determined in the soil sample No.1 was increased when the temperature increased from 30 to 60℃. The 50℃ was chosen for the late sequential extraction of the fractions of exchangeable and carbonate species of heavy metals from the soil samples since the extraction efficiencies between 50 and 60℃ were not obviously different.
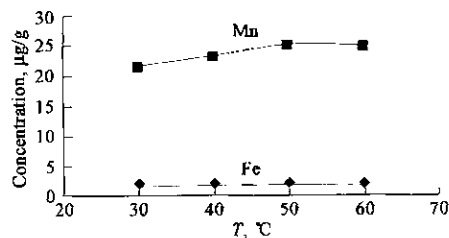

Fig.2 Effect of temperature on UE efficiency

2.4 Comparison of UE and CE

The Tessier method(Tessier, 1979) was modified and applied to the speciation analysis of Cu, Fe, Mn, Ni, Pb and Zn in the soil samples in this work. For the first two fractions of the heavy metals, i.e. the exchangeable and carbonate fractions, extracts of 0.5 mol/L $MgCl_2$(pH 7) and 0.5 mol/L NaOAc adjusted to pH 5.0 with HOAc were instead of 1 mol/L $MgCl_2$ (pH 7) and 1 mol/L NaOAc adjusted to pH 5.0 with HOAc since the slit of the air-acetylene burner was easily blocked when the 1 mol/L of the salt solutions were used. The modified Tessier method, using the optimized UE mode in this work, was applied to the species analysis of some heavy metals in the soil samples in order to reduce the extraction time for the species analysis. The extraction was carried out in triplicate and the results obtained for Cu, Fe, Mn, Ni, Pb and Zn are listed in Table 2. From Table 2 it can be seen that although the extraction time used for the first two fractions of the heavy metals species using the UE was 3 h and less than that of using the CE, which needs 6 h, the contents of Cu, Fe, Mn, Ni, Pb and Zn in the first two fractions were higher than those extracted using the CE. Comparing with the results obtained by using the CE, the extraction efficiencies for the first and second fractions of the above heavy metals in the soil sample No.1 by using the UE were 104% and 122% for Cu, 112% and 124% for Fe, 739% and 1120% for Mn, 256% and 129% for Ni, 149% and 105% for Pb, and 106% and

118% for Zn, respectively; and 166% and 221% for Cu, 176% and 183% for Fe, 167% and 111% for Mn, 252% and 289% for Ni, 223% and 166% for Pb, and 185% and 110% for Zn in the soil sample No.2, respectively. Thereby it was approved again that the extraction of heavy metal from soil by the UE for the speciation analysis has its advantages comparing with the CE because of not only less time needed but also higher extraction efficiency.

The percentages of the five fractions of Cu, Fe, Mn, Ni, Pb and Zn in the soil samples No.1 and 2 by the modified Tessier sequential extraction procedure using the UE mode were compared with the results released using the CE mode are shown in Fig.3, respectively. It can be seen that a great similarity was found between the results obtained by using both of the UE and the CE. In the soil sample No.1 the extractable Cu, Fe, Mn, Ni and Zn were mainly associated with the third fraction, i.e. the Fe-Mn oxides phase, and their percentages were 14.9%, 53.6%, 79.9%, 13.7% and 22.4% for the UE, and 18.6%, 51.5%, 81.0%, 17.6% and 22.2% for the CE, respectively; but the extractable Pb was mainly existed in the forth fraction, i.e. the organic matter phase, and the percentages were 39.4% and 40.3% for the UE and the CE, respectively. In the soil sample No.2 the extractable Cu, Ni, Pb and Zn were mainly associated with the fourth fraction; their percentages were 46.8%, 14.1%, 34.7% and 27.0% for the UE, and 40.1%, 15.2%, 33.6% and 28.4% for the CE, respectively; the extractable Fe and Mn were mainly associated with the third fraction, their percentages were 10.2% and 34.0% for the UE, and 9.9% and 53.3% for the CE, respectively. Especially for Mn and Pb, the contents of Mn in the Fe-Mn oxides and the contents of Pb in the organic matter were the highest in the five fractions for both of the soil samples No.1 and 2. This is consistent with the results reported by a number of previous studies on soils(Davidson, 1994; Dong, 1998; Ho, 2000). The high proportions of Cu, Ni and Zn in the residual fraction, about 40%—70%, and the generally low levels of extractable metals indicated that the soils are relatively unpolluted with these metals. This is maybe surprising since the samples were collected from the steel factory, which was established in 1958, and leaching of heavy metals from the site into the soils may have been considered. It is interesting that this phenomenon was also reported by Davidson *et al*. (Davidson, 1994). Generally the sum of the contents of the metals from all the five fractions was slightly less than that of the same amount of the sample digested by aqua regia directly. This perhaps caused by losing during the processes of 5 treatment steps.

2.5 Effect of concentration of $NH_2OH \cdot HCl$ on extraction efficiency

Manganese oxides in soils and sediments were found readily dissolved by a hydroxylamine hydrochloride($NH_2OH \cdot HCl$) solution. A 0.1 mol/L $NH_2OH \cdot HCl$ solution prepared in 0.01 mol/L HNO_3(pH 2) dissolves, on the average, 85% of manganese oxides from various sediments after equilibrating for 30 min and it is recommended for the extraction of manganese oxides from soils or sediments. 0.04 mol/L $NH_2OH \cdot HCl$ in 25%(v/v) HOAc was used to extract the fraction bound to Fe-Mn oxides since only slight attack of the major silicate components occurs during treatment with $NH_2OH \cdot HCl$—HOAc (Chao, 1972). Four different
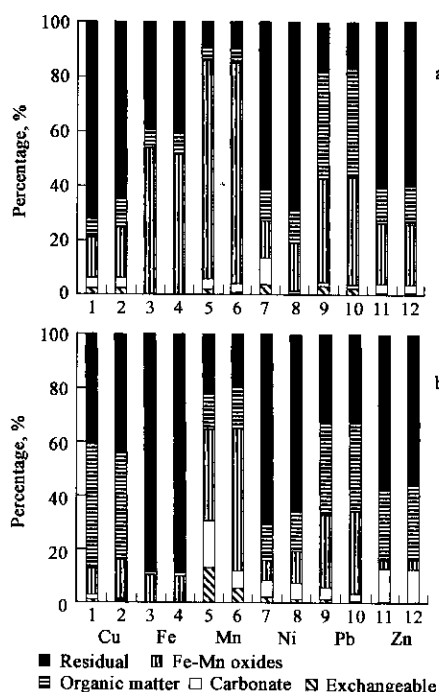
Fig.3　Comparison results between UE and CE
a: soil sample No.1; b: soil sample No.2; 1, 3, 5, 7, 9, 11: UE; 2, 4, 6, 8, 10, 12: CE

concentrations of $NH_2OH \cdot HCl$ in 25% (v/v) HOAc were tested and the results are shown in Fig.4. It is obviously seen that the released amounts of the all studied elements from the soil sample No.1 are increased along with increasing the concentration of hydroxylamine chloride in the extract solution. The released amounts of Cu, Fe, Mn, Ni, Pb and Zn extracted from the soil by 0.3 mol/L of $NH_2OH \cdot HCl$ solution were 2.8, 2.4, 1.3, 1.5, 1.3, 2.0 and 2.1 times than those extracted by 0.04 mol/L of $NH_2OH \cdot HCl$ solution, respectively. A combined solution of 0.02—1 mol/L NH_2OH ·HCl and 25% HOAc was originally devised by Chester and Hughes to investigate the partitioning of trace metals in pelagic sediments. They found that the concentration of $NH_2OH \cdot HCl$ could effectively dissolve hydrous iron and manganese oxide phases from ferro-manganese nodules(Chao, 1983). Shiowatana et al. have also reported that increasing the concentration of hydroxylamine in the reducible fraction step from 0.04 to 0.5 mol/L affected the extraction efficiency for Fe, Mn and Zn(Shiowatana, 2001).
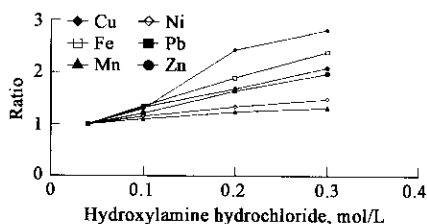

Fig.4　Effect of hydroxylamine hydrochloride concentration on extraction of heavy metal from soil
The vertical axis is the ratio of the released amount of metal by different concentration of hydroxylamine hydrochloride to the released amount of metal by 0.04 mol/L hydroxylamine hydrochloride

3　Conclusions

The ultrasonic energy by means of ultrasonic cleaning bath can be used to not only reduce the operation time but

improve the extraction efficiency for the extraction of extractable fractions of heavy metals from soil, comparing with the CE. It can be seen from the experiments that a great similarity of the operationally-defined fractions of the species for Cu, Fe, Mn, Ni, Pb and Zn in the soil samples collected from the steel factory was existent between the results obtained by using both of the UE and the CE for the modified Tessier sequential extraction procedure. The total operation time for the first four steps needed only about 8 h by using the UE, however, about 18 h by using the CE. The extraction efficiencies for the extraction of species of the heavy metals by using the UE were also better than those of the CE. The extraction efficiencies of the first and second fractions for Cu, Fe, Mn, Ni, Pb and Zn in the soil samples by using the UE were from 104% to 1120%, comparing with the results obtained by using the CE.

The extractable Cu, Ni and Zn in the soil sample No.1 were mainly associated with the third fraction, i.e. the Fe-Mn oxides phase, and fourth fraction, i.e. the organic matter fraction, in the sample No.2; the extractable Fe and Mn were all mainly associated with the third fraction, and Pb fourth fraction, in both the samples; especially for Mn and Pb, the content of Mn in the phase of Fe-Mn oxides and the content of Pb in the phase of organic matter were the highest in the five fractions, despite using the UE or the CE.

The concentration of $NH_2OH \cdot HCl$ obviously affected the extraction of the third reducible fraction of the heavy metals from the soils. The capacities of releasing the third fraction of Cu, Fe, Mn, Ni, Pb and Zn were increased from 100% to 282%, 240%, 133%, 150%, 198% and 200%, respectively when the concentration of $NH_2OH \cdot HCl$ was increased from 0.04 mol/L to 0.3 mol/L.

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