Speciation and Optimization of Multi-Elements Analysis of River Sediment in Shanghai by ICP-MS with Microwave-Assisted Digestion Method

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An analytical method was systematically developed for the multi-element analysis of Cr, Ni, Cu, Zn, Pb and Cd in sediments of Huangpu River in Shanghai by inductively coupled plasma mass spectrometry (ICP-MS) with microwave-assisted acid digestion. Three significant factors including drying method, digestion solution (volume ratio of HNO_3: HF: H_2O_2) and the presence of centrifugal separation procedure were investigated individually and compared. Results showed that drying under the temperature of 50 °C caused the largest fluctuation in final results, whereas drying under 100 °C had the least variation in detection results. Increasing the ratio of HF or H_2O_2 was beneficial for fully digestion of sediment samples. Centrifugation of the digestion solution could obtain higher detected metal concentration. Speciation of the sediment showed that the largest fraction of metals existed was residual fraction, followed by Fe-Mn oxide fraction and organic matter fraction.

Keywords: Sediment, Huangpu River, Heavy metals, Microwave-assisted digestion, ICP-MS.

INTRODUCTION

Huangpu river is the longest river in Shanghai and contributes to the largest fraction of its water supply. It has lots of tributaries such as Suzhou river, Yunzaobang, *etc.* and around other 50 rivers. About 80 % of drinking water in Shanghai comes from Huangpu river. Since 1990s, the rapid development of industry brought about many negative effects on human health, people got affected through exposure to environmental pollutants. Heavy metals in Huangpu river are one of the most important contaminants, which are refractory and persistent in the environment[1]. Heavy metals transported through different sediment components in various ways such as ion exchange, adsorption, with an average suspended sediment level of 544 mg/L[2]. Sediment, especially suspended sediments are reported to consist of a wide range and complex distributions of heavy metals[3]. Besides, uncontrolled inputs can increase the burden on biochemical cycling in the ecosystem[4]. Most of the heavy metals like Hg, Cd, Cr, Pb are toxic to human and aquatic lives even at very low concentrations. Therefore the elemental-analysis of river sediments had drawn serious attention, especially from the point of environment investigation[5].

Nowadays, the most commonly used techniques in detection of heavy metals in river sediments are inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS). Usually ICP-OES has low sensitivity for trace metals analysis. Atomic absorption spectrometry is labor consuming and time consuming, for multi-elemental analysis under certain circumstance, where many operational steps and lots of repetitive work are required to analyze different elements in samples at very low concentrations.

Inductively coupled plasma mass spectrometry (ICP-MS) was chosen to detect the content of heavy metals in river sediment since it is faster, more precise and effective[6]. Besides the rapid processing for multi-element detection, ICP-MS also offers simultaneous determination of numerous elements with a large dynamic range that overlaps the concentration ranges of atomic absorption spectrometry methods, as well as high sensitivity, rapid mass scanning and short analysis time[7].

At the same time, sample preparation is one of the most vital links in characterization of river sediment because it is insoluble and persistent. These techniques require decomposition of the sediment sample and metals transformation into a homogeneous liquid phase. One of the most commonly used methods is wet digestion. In this method, the mixture of sediment samples and concentrated nitric acid is heated in an open glass container to dryness with an infrared lamp and the remaining organic carbon is combusted in a muffle furnace at 525 °C. Then the non-organic residue is digested with concentrated nitric acid, vapored to dryness and diluted with 5 % (v/v) nitric acid. These sample preparation methods, however, have

several disadvantages such as time consuming, possibilities of components loss, contamination and low recovery of elements extraction[8].

Microwave-assisted decomposition processes have been used in the pretreatment of a variety of samples for its time saving characteristic that microwave energy could be used to obtain necessary decomposition temperature easily. Moreover, this method causes less contamination[9]. Especially digested under pressure in polytetrafluoroethylene (PTFE) closed-vessels, complete metal recovery is generally achieved. The advantages of pressure digestion in closed-vessels over the conventional open glass vessel digestion methods include higher speed in sample decomposition and lower risks of contamination and volatilization[10].

Based on microwave-digestion with closed vessels, different acid mixtures are used for digestion in various researches. HNO_3-HCl-HF-H_2O_2, HNO_3-HCl-HF-$HClO_4$, HNO_3-HF-H_2O_2, HNO_3-HCl and HNO_3-HF are the main stream of acid system. Due to the low boiling point (122 °C) of concentrated nitric acid (HNO_3), organics and many other matrixes cannot be decomposed by the concentrated nitric acid alone, unless digesting for longer time or with strong oxidant such as hydrogen peroxide. Although $HClO_4$ has strong oxidation, mixture with $HClO_4$ in closed vessels could lead to explosion and cause danger. Besides, ICP-MS detection might be interfered by numerous chlorines and HCl in the final sample matrix. Hence, $HClO_4$ and HCl should be avoided. In addition, SiO_2 is found to account for 30-90 % in sediment samples. So in the preliminary treatment, hydrogen fluoride (HF) by which Si compounds could be dissolved and transformed into the formation of volatile SiF_4 should be added. Thus for digesting the sediment samples, the combination of concentrated nitric acid, hydrofluoric acid and hydrogen peroxide are suggested.

In this study, the influence of three process factors (drying method, the volume ratio of concentrated nitric acid: hydrofluoric acid: hydrogen peroxide and centrifugal separation procedure) of microwave digestion are studied and compared based on the heavy metals (Cr, Ni, Cu, Zn, Pb, Cd) recovery to find a most effective combination for sediment sample preparation. Speciation of the metals in the sediment was also conducted.

EXPERIMENTAL

Sampling and sample pretreatment: Sediment sample was collected from the bottom of the Huangpu river which is arched across by Songpu bridge (30°58'10.4" N, 121°18'22.7" E). The wet sediment samples were sealed in PTFE bags with ice bags during sampling and kept in refrigerated in ultra storage freezer (-20 °C) when back to lab in order to prevent changes in heavy metal distribution among different phases.

Deionized water (conductivity 18.2 MO) supplied by Milli-Q Advantage system associated with Q-pod Element system was used throughout all procedures. Concentrated (65 % w/v) nitric acid (Merck, Darmstadt, Germany), high-quality (48 % w/v) hydrofluoric acid (Merck, Darmstadt, Germany), 30 % (w/v) hydrogen peroxide, $MgCl_2$, CH_3COONa, $NH_2OH \cdot HCl$, CH_3COOH and CH_3OONH_4 (Sinopharm Chemical Reagent Co., Ltd) were used for analyses. The standard solutions used

for calibration were prepared from quality control standard (PerkinElmer, United States, 100 mg/L) by successive dilutions with Milli-Q water.

Preliminary treatment procedure: Nitric acid is generally used to decompose biological samples, metals and alloys. Hydrofluoric acid and hydrogen peroxide were employed to ensure the complete dissolution of silicone components and to acquire an effective and rapid digestion of the sediment samples[11]. Dried and sifted sample (0.1 g) was treated for about 1 h for preliminary digestion mixed with nitric acid, hydrofluoric acid and hydrogen peroxide (total volume 5 mL) in order to release the gases produced initially by the mixture and to eliminate the influence of an excessive increase in pressure in PTFE closed-vessels. Next, the mixtures were digested in the microwave digestion system, then the digested samples and PTFE vessels were heated together at the temperature of 150 °C for 3-5 h in an acid-driven processor to avoid the quartz-corrosion attributed to hydrofluoric acid.

The TOPEX (PreeKem) closed-vessel microwave digestion system was used for sediment sample preliminary treatment. The operational conditions and heating program used were carried out according to the conditions recommended by the manufacturer as follows: 160 °C for 3 min under the pressure of 15 atm, 190 °C for 4 min under the pressure of 18 atm, 210 °C for 15 min under the pressure of 22 atm.

After digestion, the solutions were diluted to a final volume of 100 mL, stored in cleaned polyethylene volumetric flask (soaked for 24 h in 10 % HNO_3 and cleaned with Milli-Q water before use). PTFE closed vessels were carefully cleaned, soaked for 24 h in 10 % HNO_3 and cleaned with Milli-Q water before use. In this work, three significant preliminary treatment factors, drying method, microwave digestion method and centrifugal separation, were investigated to optimize the analyzing of multi-elements in river sediment. For drying method, a total of 3 ways of drying were employed: drying under 50 °C for 48 h, drying under 100 °C for 48 h and freeze-drying. For microwave digestion method, 4 different HNO_3:HF:H_2O_2 volume ratios were studied: 3:1:1, 6:1:1, 3:2:1 and 3:1:2. For the diluted digestion solutions, the effects of centrifugal separation on the final results were also investigated. Each experiment was replicated for 5 times.

Speciation of the six heavy metals: The speciation of the six heavy metals was studied by Tessier procedures. The procedure is elaborated as follows and shown in Fig. 1.

Step 1: Exchangeable fraction (EXC): 2 g dried and sifted sediment sample was extracted with 16 mL of 1 mol/L $MgCl_2$ (pH = 7) in a 50 mL centrifuge tube for 1 h under the temperature of 25 °C with continuous vibration, then the mixture was centrifuged for 20 min at 4000 rpm. The supernatant liquor was filtered through 0.45 μm filter head, acidized and kept at 4 °C. The residue was washed with deionized water, centrifuged (20 min, 4000 rpm) and prepared for the next step. Each step was operated twice.

Step 2: Carbonate bound fraction (CARB): The residues left from step 1 was extracted with 16 mL of 1 mol/L sodium acetate (25 °C, pH = 5) for 8 h with continuous vibration, then centrifuged (20 min, 4000 rpm). The supernatant liquor was filtered through 0.45 μm filter, acidized and kept at 4 °C. The residue was washed for next step.
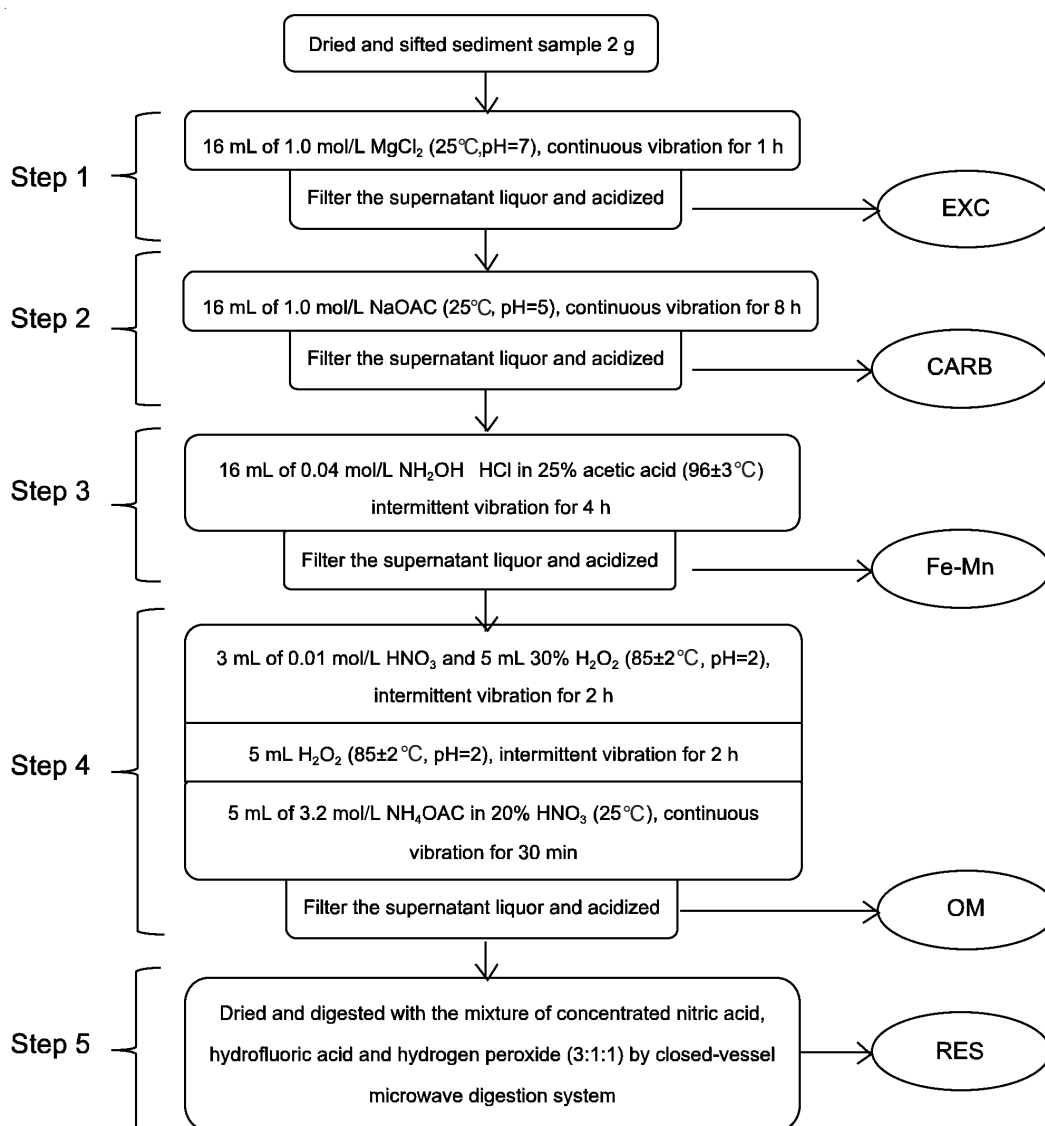
Fig. 1. Tessier procedures for speciation

Step 3: Fe-Mn oxide fraction: The residues was extracted with 16 mL of 0.04 mol/L $NH_2OH \cdot HCl$ in 25 % acetic acid for 4 h under the temperature of 96 ± 3 °C with intermittent vibration, then centrifuged (20 min, 4000 rpm). The supernatant liquor was filtered through 0.45 μm filter, acidized and kept at 4 °C. The residue was for next step.

Step 4: Organic matter (OM) bound fraction: The residues was extracted with 3 mL of 0.01 mol/L HNO_3 and 5 mL 30 % H_2O_2 for 2 h (85 ± 2 °C, pH = 2) with intermittent vibration; another 5 mL H_2O_2 was added again with intermittent vibration for 2 h (85 ± 2 °C, pH = 2); and 5 mL of 3.2 mol/L NH_4OAC in 20 % HNO_3 was added with continuous vibration for 0.5 h at 25 °C, then centrifuged (20 min, 4000 rpm). The supernatant was filtered through 0.45 μm filter head, acidized and kept at 4 °C.

Step 5: Residual fraction (RES): Residues from step 4 were dried and digested with the mixture of concentrated nitric acid, hydrofluoric acid and hydrogen peroxide (3:1:1) by closed-vessel microwave digestion system. Then the digested solution was diluted to a final volume of 100 mL

in cleaned polyethylene vessels, acidized and kept at 4 °C. All the filtered solutions from each step were detected by ICP-MS.

Instrument: The ICP-MS (NexION300, PerkinElmer, United States) was used for detection of target metals in preliminary treated samples. The isotopes of metals used for determination and calculation were ^{52}Cr, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{208}Pb and ^{111}Cd. In order to exclude the contamination of the digestion procedure and sample manipulation, a blank solution was prepared and used throughout every step of analyses. Operational conditions are as follows: RF power: 1100 watts, Plasma gas flow rate: 15 L/min, Auxiliary gas flow rate: 1.2 L/min, Nebulizer gas flow rate: 0.93 L/min, Sampler and skimmer cones: Nickel, Time of sweeps: 20 msec, Number of replicates: 3.

RESULTS AND DISCUSSION

Calibration and the limit of detection: It was noticeable to monitor the linearity by using calibration curve and checking of limit of detection (LOD) could ensure the reliable results in each analytical procedure[12]. The instrumental method

parameters were characterized by the determination of each metal (Cr, Ni, Cu, Zn, Pb and Cd) through the analysis of blanks and successive diluted standards solutions. The LOD were determined as well. A summary of these results is provided in Table-1. The results show that the response of instrument can be regarded linear in the ranges studied. In all cases the correlation coefficients were greater than 0.999.

TABLE-1
DETERMINATION OF Cr, Ni, Cu, Zn, Pb AND Cd

Element	LOD (mg/L)	Liner equation	R^2
Cr	1.9×10^{-4}	$Y = 3 \times 10^{-5} x - 0.2465$	0.99992
Ni	1.1×10^{-4}	$Y = 1 \times 10^{-4} x + 0.0094$	0.99982
Cu	1.0×10^{-4}	$Y = 6 \times 10^{-5} x + 0.036$	0.99997
Zn	3.4×10^{-4}	$Y = 2 \times 10^{-4} x - 0.8936$	0.99946
Pb	3.8×10^{-4}	$Y = 4 \times 10^{-5} x - 0.0751$	0.99987
Cd	1.0×10^{-5}	$Y = 2 \times 10^{-4} x - 0.0115$	0.99992

Speciation results of the 6 heavy metals in Huangpu river sediment: Heavy metals in sediments are bound to various geochemical fractions with different strengths[13]. The dominant forms of heavy metals accumulated in the sediments could be divided into the following five basic categories: exchangeable fraction, carbonate fraction, Fe-Mn oxide fraction, organic matter fraction and residual fraction[14]. It is possible for different fractions of metals, which were discharged from industrial plants and factories such as smelting industry and plating industry, to settle along the river sediment[15]. Diverse heavy metal speciation in the sediments may lead to various detection results[16].

The results in Fig. 2 indicated that the fraction of Cr mainly consists of residual fraction, organic matter fraction and Fe-Mn oxide fraction oxide fraction, as residual fraction (85.5610 %) > organic matter fraction (8.2772 %) > Fe-Mn oxide fraction (6.0566 %). The exchangeable fraction and carbonate fraction contributed for only 0.0667 and 0.0385 % of all Cr content. The Fe-Mn oxide fraction and organic matter fraction of Cr was mainly contained in the sediments. The form Fe-Mn oxide fraction is thermodynamic unstable, organic matter fraction is easy to be degraded, as a result the composition and speciation of Cr may change or loss due to a higher temperature. For Ni, the fraction distribution was residual fraction > Fe-Mn oxide fraction > organic matter fraction > exchangeable fraction > carbonate fraction. For Cu, the speciation result was residual fraction > organic matter fraction > carbonate fraction > Fe-Mn
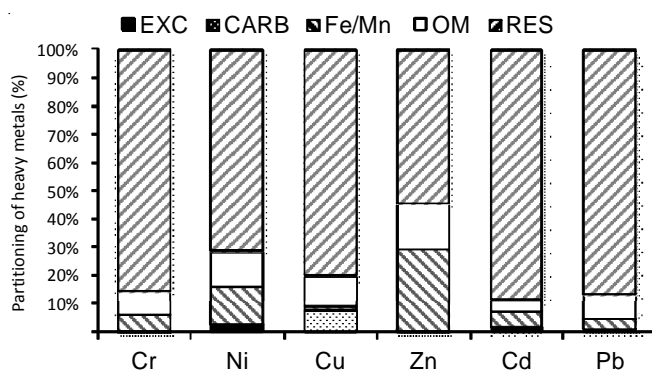
oxide fraction > exchangeable fraction. For Zn, the condition was residual fraction > Fe-Mn oxide fraction > organic matter fraction > exchangeable fraction > carbonate fraction. The condition of metals Cd and Pb was similar.

Detection results of six metals with different preliminary treatment procedures: The combinations of the three significant factors in preliminary treatment procedure were considered and each sediment sample was prepared and analyzed. The results were shown in Fig. 3. It could be observed that different preliminary treatment procedures brought about varied detection results. For Cr, the preliminary treatment condition of drying at 50 °C, HNO_3:HF:H_2O_2 ratio of 6:1:1 with centrifugal separation led to the maximum detected metal concentration of 0.1673 mg/g, the minimal concentration of 0.0912 mg/g was obtained under the condition of drying at 50 °C, HNO_3:HF:H_2O_2 ratio of 3:1:2 without centrifugal separation. In addition, it could be observed that the treatment of drying under 50 °C caused the largest fluctuation in final results; the treatment of drying under 100 °C had the most consistent and stable results, which achieved the maximum concentration of 0.1462 mg/g and the minimal concentration of 0.1038 mg/g. When using freeze-drying, the detected concentrations increased with the proportion of HF and H_2O_2.

Drying under 50 °C may cause incomplete or uneven loss of water and metal fractions, thus the treatment of drying under 50 °C induced the results with the greatest variation. Freeze drying usually cause less damage to the samples than using higher temperatures and preserve the purpose substance to the most extend, considering the unnegligible organic matter fraction, more hydrofluoric acid or hydrogen peroxide was needed in order to digest samples completely. Additionally, more concentrated nitric acid may help to dissolve more heavy metal out.

In most of the cases, the obtained concentration of the pretreated sample with centrifugal separated process was higher than the sample without centrifugal separation. That means the centrifugal separated process was an important step for digested sample detection. It is likely that a small part of the solid grains remained in the digested mixture might absorb little fractions of metals and accumulated at the bottom of the volumetric flask, therefore the concentration of pretreated sample was reduced.

From the experimental results, it was recommended to employ the condition of drying under 100 °C, HNO_3:HF:H_2O_2 ratio of 3:1:2 and centrifugation of the digested solution as the optimized method for sediment digestion. The detection results of other 5 metals had analogous tendency, as indicated in Figs. 2 and 3, which certified the reliability of this study.

Finally the recoveries of each elements were determined using standard sample containing Cr (0.4 mg/g), Ni (0.1 mg/g), Cu (0.4 mg/g), Zn (0.4 mg/g), Pb (0.1 mg/g) and Cd (0.001 mg/g), under the optimized condition and the detected concentrations of Cr, Ni, Cu, Zn, Pb and Cd containing in dried sediment were 0.46623, 0.16657, 0.54596, 0.78530, 0.12590 and 0.001484 mg/g, respectively, thus the obtained recoveries for Cr, Ni, Cu, Zn, Pb and Cd were 80, 92.79, 102.94, 106.8, 92.67 and 84.40 %, respectively, which further proved the feasibility of this method.
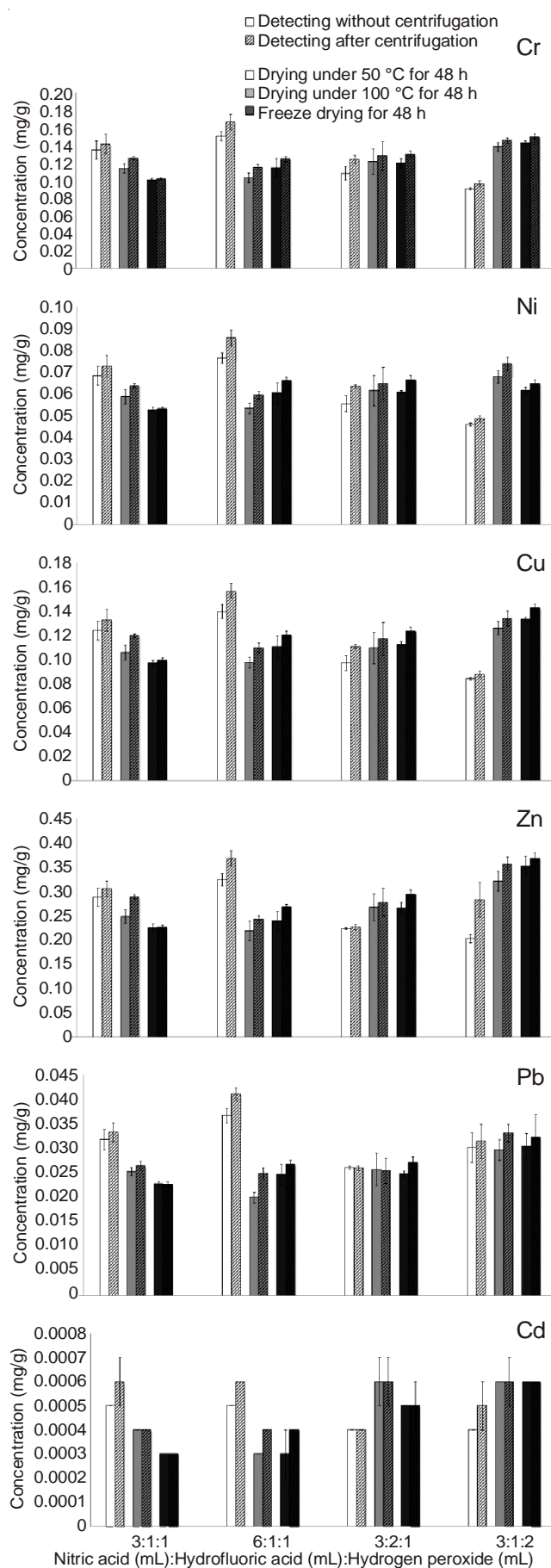

Fig. 2. Speciation results of the 6 heavy metals in Huangpu river sediment

Fig. 3. Detected concentrations of 6 metals in Huangpu river sediment with different preliminary treatment procedures

Conclusion

This study introduced a feasible digestion method for river sediments. This method digested sediment sample with the assistance of microwave, the impact of three factors including drying method, the volume ratio of concentrated nitric acid, hydrofluoric acid and hydrogen peroxide, the presence of centrifugal separation procedure on the detection result of 6 metals was investigated. The result indicated that drying temperature of 50 °C brought about the largest fluctuation, whereas drying under 100 °C had the least variation in detection results. Increasing the ratio of HF or H_2O_2 could digest the sediment more completely. The presence of centrifugal separation procedure for the digestion solution usually led to higher detected metal concentration. Speciation of the sediment showed that the largest fraction of metals existed was residual fraction, followed by Fe-Mn oxide fraction and organic matter fraction, a small amount of exchangeable fraction and carbonate fraction were also existed in the sediment samples.

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