Differentiation of digestion method for heavy metals in river sediments based on organic matter gradients

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Abstract. Heavy metal detection in river sediments is critical in evaluating heavy metal pollution levels, risk and control in these matrices. Most of existing detection methods have the disadvantage of low recovery rate and high total acid consumption. Due to continuous accumulation of metal and relative high content of organics in river sediments, this paper focused on studying differentiated digestion method of heavy metals based on organics gradient grading. Surface river sediment samples were collected from 26 different rivers and lakes within the Qiantang River basin (e.g. Hangzhou and Jiaxing). Organic matter content in these samples were tested and these samples were divided into 8 groups according to content of organic matter. This was followed by testing the effects of hydrochloric acid, nitric acid and hydrofluoric acid on the digestion of heavy metals (Cu, Zn and Ni). The optimum digestion system of heavy metals in river sediments based on organic matter gradients was established. Results demonstrated that digestion system can achieve high recovery rate (90%~110%) and an average detection accuracy, while total acid consumption is about 10.54 mL, which is less than that of the Chinese standard digestion method (19mL). This means that the digestion system proposed in this paper is environmentally friendly.

1. Introduction

With the industrial development and population growth, the environmental pollution caused by industrial wastewater and domestic sewage is becoming increasingly serious and urban river pollution is intensifying gradually. River sediment is an important component of water ecological environment. Sediments act as a reservoir of pollutants, could absorb pollutants from water. But benthic and pelagic organisms are at a greater risk due to the accumulative effects of pollutants sorbed onto sediments [1, 2]. Sediment is a main living place and food source of benthos. Pollutants in sediments could access into terrestrial biota and human bodies through biological concentration and food chain.

Urbanization, industrialization and intensive agricultural development are main factors which result an increase of heavy metal content in river sediments. Due to the toxicity, durability and undegradability of heavy metals, it has become a major pollutants that influence sediment quality significantly [3] and also cause biological damage. Therefore, it is necessary to detect heavy metals in river sediments in order to evaluate heavy metal pollution level and corresponding potential risks [4, 5]. At present, it often adopts the soil heavy metal detection method in the Chinese standard [6, 7] is used to determine heavy metal content in river sediments. This method includes sample digestion, which plays a vital role in detection of heavy metals. Traditional digestion methods aims at obtaining heavy metals content, including free and mineral combined ones. The latter are difficult to
decomposed due to their high stability and bio-availability. Organic matter combined heavy metals are another kind of important morphology of soil heavy metals. Results demonstrated the content of this kind of heavy metals correlated with organic matter content [8, 9] and heavy metals mainly accumulate in organics.

Different acids play different roles in the process of heavy metal digestion. Hydrochloric acid is for preliminary digestion. Nitric acid, an oxidizing acid, is the dominant acid of digestion. It is the common acid used to oxidize organic matter samples. Hydrofluoric acid is to break down silicate combined metals that are in difficult-to-melt lattice system in sediment minerals. As an inoxidizability acid with strong complexing power, it is often used to analyze inorganic samples and could dissolve silicate. Perchloric acid which has high boiling point and strong oxidability are used to not only expel residual hydrofluoric acid and prevent hydrofluoric acid to corrode glass apparatus but also digest remained organics.

Through analysis on differentiation of digestion method for heavy metals in river sediments based on organic matter gradients, the optimum digestion system for heavy metals in river sediments based on organic matter gradients was proposed in this paper. It can improve recovery rate and detection accuracy of heavy metals in sediments. It is also more convenient and environmentally-friendly, which includes less acid-consumption.

2. Materials and methods

2.1. Sampling site layout

Sampling sites were located Hangzhou and Jiaxing along the Qiantang River and selected based on the type and water quality differences. Spatial distribution of sampling sites is shown in Table 1.

| No. | Longitude and latitude | Latitude | Longitude |
|-----|------------------------|----------|-----------|
| 1   | 30°39′15″ 120°31′49″   | 10       | 30°04′36″ 120°12′03″ |
| 2   | 30°14′49″ 120°07′40″   | 11       | 30°07′49″ 120°12′44″ |
| 3   | 30°01′41″ 120°01′03″   | 12       | 30°19′27″ 120°08′57″ |
| 4   | 30°01′39″ 120°00′28″   | 13       | 30°09′09″ 120°13′52″ |
| 5   | 30°14′50″ 120°07′37″   | 14       | 30°13′48″ 120°08′11″ |
| 6   | 30°06′16″ 120°12′58″   | 15       | 29°39′02″ 119°04′42″ |
| 7   | 30°06′02″ 120°12′49″   | 16       | 29°27′52″ 119°15′28″ |
| 8   | 30°15′33″ 120°03′44″   | 17       | 30°06′43″ 120°11′13″ |
| 9   | 30°39′15″ 120°31′49″   | 18       | 30°03′23″ 119°57′38″ |

2.2. Sampling and processing

Superficial sediment samples were collected with piston samplers (Figure 1) and kept in sealed bags with labels. In laboratory, all samples were naturally air-dried in cool and ventilate places. Bulk materials including like gravels, animal and plant residues were removed manually. Later, they were tiled on a piece of solid fiberboard and pressed with a piece of glass rod. Samples were sieved by a 20-mesh sieve and oversize substances were removed. Sifted samples were divided through quartering sample and then these samples were ground by an agate mortar until all of them could be sifted by a 100-mesh sieve. Processed samples were sealed up for the following tests.
2.3. Sample grouping based on organic matter gradients

Total organic carbon (TOC) content of 26 samples were tested by using the infrared carbon-sulphur method [10]. Organic matter (OM) and TOC could be transformed mutually according to Equation (1):

$$m_{OM} = 1.724 \times m_{TOC}$$  \hspace{1cm} (1)

TOC content of 26 sediment samples are shown in Figure 2. Since OM and TOC could be transformed mutually according to Equation (1), this paper applied TOC gradient instead of OM gradient for the analysis convenience. It can be seen from Figure 2 that the average TOC content of 26 samples is 2.34% and the average OM content is 40.42 g/kg. The highest TOC content (13.27%) is achieved by Sample 2, while the lowest (0.49%) is at Sample 15. This reflects that sediments in different water environments have significant different in OM content. In this paper, samples were divided into 8 groups according to natural gradient of OM content (Tab. 2). In Tab. 2, 7 samples were actually collected from rivers while the other one was a man-made sample with 10% OM content. They represented river sediment samples of different OM gradients for the discussion of optimum digestion system for Cu, Zn and Ni.

Table 2. OM gradient-based grouping of river sediment samples.

| Group No. | Representative sample No. | TOC content(%) | Organic content(g/kg) | OM gradient(g/kg) |
|-----------|---------------------------|----------------|-----------------------|-------------------|
| 1         | 15                        | 0.49           | 8.45                  | 0~8.45            |
| 2         | 22                        | 0.69           | 11.90                 | 8.45~11.90        |
| 3         | 12                        | 0.99           | 17.07                 | 11.90~17.07       |
| 4         | 13                        | 2.54           | 43.79                 | 17.07~43.79       |
| 5         | 3                         | 5.66           | 97.58                 | 43.79~97.58       |
| 6         | 5                         | 7.56           | 130.33                | 97.58~130.33      |
| 7*        | Man-made                  | 10             | 172.40                | 130.33~172.40     |
| 8         | 2                         | 13.27          | 228.77                | 172.40~228.77     |

Note: *This sample is the mixture of two samples with 5.66% TOC and 13.27% TOC at a mass ratio of 3.27:4.34.

2.4. Experimental design

2.4.1. Influence tests of digestion system factors on heavy metal digestion. Five samples (0.4g ± 0.0002g for each) of every sample in Table 2 were taken and put in PTFE crucible, respectively. Only the influence of hydrochloric acid, nitric acid and hydrofluoric acid on digestion were studied. Perchloric acid has extremely strong oxidability and is used to decompose organics that haven’t been
digested by other acids. However, it is unnecessary to digest these organics due to their low environmental availability.

The addition of acids was done in the following configuration:

Digestion system 1: only hydrochloric acid (2 mL, 4 mL, 6 mL, 8 mL, 10 mL) was added into samples.

Digestion system 2: only nitric acid (2 mL, 4 mL, 6 mL, 8 mL, 10 mL) was added into samples.

Digestion system 3: firstly, 6 mL hydrochloric acid was added into samples and then nitric acid (2 mL, 4 mL, 6 mL, 8 mL and 10 mL) was applied.

Digestion system 4: firstly 6 mL hydrochloric acid and 5 mL nitric acid were added into samples and add hydrofluoric acid (2 mL, 4 mL, 6 mL, 8 mL, 10 mL) finally, added 3 mL perchloric acid.

Samples were then heated on a hot plate at 100 °C to reduce the acid volume to 2 mL. After it cooled down, add a combination of a certain volume of nitric acid (HNO₃ [69%]), a certain volume of hydrofluoric acid (HF [48%]) and 3 mL perchloric acid (HClO₄ [70%]) on a hot plate at between 120 and 150 °C until it became nearly dry. The digested solution of sediment was diluted with deionized water and filtered quantitatively into a 50-mL volumetric flask. The heavy metal contents (Cu, Zn and Ni) in the sediment samples after pretreatment were detected by an atomic absorption spectrometer (AA-6300, Shimadzu, Japan) with an air/acetylene flame and acetylene (0.09 MPa) as the auxiliary gas at a pressure of 0.4 Mpa.

The optimum digestion system was determined using the equation(s)

\[ VS = \min \{V_{HCl} + V_{HNO₃} + V_{HF} + V_{HClO₄}\} \]

\[ STOC = \{V_{HCl}, V_{HNO₃}, V_{HF}, V_{HClO₄}\} \]

where, VS is total acid consumption of the digestion system, STOC the optimum digestion system under a certain TOC, V and min is the volume of acid and the minmum of the total.

By studying the effects of different acids on the digestion of heavy metals in the system, the sensitivity of different gradient samples to different acids can be determined. At the same time, it can also provide reference for the best digestion method for different organic content samples.

1) Influence test of hydrochloric acid on heavy metal digestion

Five samples (0.4 g±0.0002 g for each) of every sample in Table 2 were taken, and put in (PTFE) crucible, respectively. 2, 4, 6, 8 and 10 mL hydrochloric acid were added into samples respectively, then heat them on the hot plate. Heavy metal content was tested according to Chinese standard methods (GB/T 17138-1997).

2) Influence test of nitric acid on heavy metal digestion

Five samples (0.4 g±0.0002 g for each) of every sample in Table 2 were taken and put in PTFE crucible, respectively. We added 2, 4, 6, 8 and 10 mL nitric acid in samples respectively, and digest them on the hot plate. Test method was the same as above.

3) Influence test of hydrofluoric acid on heavy metal digestion

Five samples (0.4 g±0.0002 g for each) of every sample in Table 2 were taken and put in PTFE crucible, respectively. We added 6 mL hydrochloric acid and digested them on the hot plate until there’s only 2 mL solution left. Then, we added 5 mL nitric acid and 30 min later, added 2, 4, 6, 8 and 10 mL hydrofluoric acid. Finally, added 3 mL perchloric acid. Test method was the same as above.

2.4.2. Determination design of the optimum digestion system. Based on test results (Figure 3, Figure 4 and Figure 5) of hydrochloric acid, nitric acid and hydrofluoric acid in digesting heavy metals in river sediment samples, samples with low organic content could be digested by adding appropriate amount of hydrochloric acid and those with high organic content could be digested by appropriate amount of nitric acid. Dosage of hydrofluoric acid shall be determined according to properties of samples and excessive dosage can lead to the loss of heavy metals. Key factors determining heavy metal digestion include digestion time, temperature and system. In these experiments, digestion time and temperature were determined according to practical situations in order to achieve the optimum reaction. This paper emphasized on Cu, Zn and Ni digestions under four digestion systems.
3. Results and discussion

3.1. Influences of digestion system factors on heavy metal digestion

(1) Influence of hydrochloric acid on heavy metal digestion

Influence of hydrochloric acid on Cu digestion is shown in Figure 3. In digestion system 1, samples with low TOC is very sensitive to hydrochloric acid volume and Cu digestion fluctuates violently. In Figure 3, it is suggested that the maximum and minimum values of Cu digestion are 10mg/kg and 40mg/kg, respectively. While results of samples with high TOC (5.66~13.27) is relatively stable, the difference is less than 5 mg/kg. It can be concluded that is due to the weak oxidability of hydrochloric acid which means it can only dissolve substances with simple structures. Thus, appropriate amount of hydrochloric acid is enough for sediment samples with low OM.

(2) Influence of nitric acid on heavy metal digestion

Influence of nitric acid on Cu digestion is shown in Figure 4. From the overall trend, Cu content in digestion solution improves gradually with the increase of amount of nitric acid. Cu digestion content reaches a peak and then decreases with the further increase of nitric acid. From the results of experiments, we can found out that digestion capacity in this system can be improved by nitric acid, which means different forms of heavy metals were decomposed gradually. Thus in the digestion solution, heavy metal content increase. However, excessive nitric acid will prolong digestion time and some heavy metals will be carried away with evaporation of exhaust gas. Consequently, heavy metal content in digestion solution decreases.

(3) Influence of hydrofluoric acid on heavy metal digestion

Influence of hydrofluoric acid on Cu digestion is shown in Figure 5. When TOC=5.66 and TOC=13.27, Cu content in digestion solution increases continuously and then achieves a stable level with the increase of hydrofluoric acid. For other samples, Cu content declines with the increase of hydrofluoric acid. Experimental results suggested partial dissolved Cu could be carried away with evaporation of exhaust gas due to excessive hydrofluoric acid.

3.2. Determination of the optimum digestion system

In this study, we take digestion results when TOC=0.69 for example. It is showed in Figure 6 that Cu content increases firstly and decreases gradually under all digestion systems. In digestion system 1, Cu content in digestion solution shows similar situation to the overall trend and reaches the peak after adding 8mL hydrochloric acid, 8mL nitric acid, 4mL nitric acid respectively and 8, 4, 10mL VS respectively. In digestion system 4, Cu content reaches the peak after adding 6mL hydrofluoric acid and 20mL VS to the system. Figure 7 shows that Zn digestion under different digestion systems (TOC=0.69) and Figure 8 shows that Ni digestion under same conditions. The rest of the results were obtained using the same analytical method.

Optimum dosage of acid under every system could be concluded from Figure 6, Figure 7 and Figure 8 and results are listed in Table 3. It can be suggested from Table 3 that recovery rate of digestion system 1, digestion system 2 and digestion system 3 varies between 89.29%~107.82%, while the recovery rates of digestion system 4 and the national standard method are relatively low. Excessive acid usage is the major reason that cause low recovery rates of digestion system 4 and the standard method. Excessive acid will prolong digestion time greatly and thereby cause heavy metal losses. Recovery rate of different digestion systems was compared and the digestion system with satisfying recovery rate and minimum VS was recognized as the optimum digestion system. The results are listed in Table 4.

As shown in Table 4, VS usage of optimum digestion systems ranges from 2~19 mL and the average amount of VS is 10.54 mL, less than that of the Chinese standard digestion method (19 mL). Therefore, the optimum digestion system not only achieves higher recovery rate and detection accuracy of heavy metals but also reduces acid consumption, which conforms to environmental protection.
Figure 3. Effect of HCl on Cu digestion.

Figure 4. Influence of HNO₃ on Cu digestion.

Figure 5. Influence of HF on Cu digestion.

Figure 6. Cu content (TOC=0.69).

Figure 7. Zn content (TOC=0.69).

Figure 8. Ni content (TOC=0.69).
Table 3. Detection results of heavy metals under different digestion systems (TOC=0.69).

| Digestion system | Heavy metals | Content (mg/kg) | Digestion systems (mL) | Recovery rate (%) |
|------------------|--------------|-----------------|------------------------|-------------------|
| Chinese standard | Cu           | 34.96           | Hydrochloric acid 6     | 80.33             |
|                  | Zn           | 252.14          | Nitric acid 5           | 81.46             |
|                  | Ni           | 45.29           | Hydrofluoric acid 5      | 89.22             |
|                  | Cu           | 40.04           | Perchloric acid 3        | 105.29            |
| System 1         | Zn           | 113.61          | VS 0                    | 96.85             |
|                  | Ni           | 85.15           | 0                       | 89.29             |
|                  | Cu           | 38.36           | 0                       | 102.21            |
| System 2         | Zn           | 797.82          | VS 0                    | 98.96             |
|                  | Ni           | 166.10          | 0                       | 107.82            |
|                  | Cu           | 35.03           | 0                       | 98.24             |
| System 3         | Zn           | 879.15          | VS 0                    | 96.58             |
|                  | Ni           | 96.31           | 0                       | 92.13             |
|                  | Cu           | 36.71           | 0                       | 91.35             |
| System 4         | Zn           | 233.83          | VS 0                    | 82.51             |
|                  | Ni           | 73.37           | 0                       | 91.79             |

Table 4. Optimum digestion systems for sediment samples with different TOC.

| TOC gradient | Heavy metals | Digestion systems(mL) | VS(mL) |
|--------------|--------------|------------------------|--------|
|              |              | Hydrochloric acid      | Nitric acid | Hydrofluoric acid | Perchloric acid |
| 0-0.49       | Cu           | 6                      | 0        | 0                 | 0             | 6       |
|              | Zn           | 6                      | 8        | 0                 | 0             | 14      |
|              | Ni           | 2                      | 0        | 0                 | 0             | 2       |
|              | Cu           | 0                      | 4        | 0                 | 0             | 4       |
| 0.49-0.69    | Zn           | 6                      | 4        | 0                 | 0             | 10      |
|              | Ni           | 0                      | 6        | 0                 | 0             | 6       |
|              | Cu           | 6                      | 8        | 0                 | 0             | 14      |
| 0.69-0.99    | Zn           | 6                      | 2        | 0                 | 0             | 10      |
|              | Ni           | 0                      | 8        | 0                 | 0             | 8       |
|              | Cu           | 0                      | 6        | 0                 | 0             | 6       |
| 0.99-2.54    | Zn           | 6                      | 4        | 0                 | 0             | 4       |
|              | Ni           | 8                      | 0        | 0                 | 0             | 8       |
|              | Cu           | 0                      | 10       | 0                 | 0             | 10      |
| 2.54-5.66    | Zn           | 0                      | 10       | 0                 | 0             | 10      |
|              | Ni           | 4                      | 0        | 0                 | 0             | 4       |
|              | Cu           | 6                      | 5        | 2                 | 3             | 16      |
| 5.66-7.56    | Zn           | 6                      | 4        | 0                 | 0             | 10      |
|              | Ni           | 6                      | 5        | 5                 | 3             | 19      |
|              | Cu           | 6                      | 6        | 0                 | 0             | 19      |
| 7.56-10.00   | Zn           | 6                      | 4        | 0                 | 0             | 10      |
|              | Ni           | 6                      | 5        | 5                 | 3             | 19      |
|              | Cu           | 6                      | 6        | 0                 | 0             | 12      |
| 10.00-13.27  | Zn           | 6                      | 10       | 0                 | 0             | 16      |
|              | Ni           | 6                      | 5        | 5                 | 3             | 19      |
4. Conclusions
Focusing on some sections of the Qiantang River in China, this study collected in a total of 26 sediment samples from river and lake branches. Firstly, these 26 sediment samples were detected about TOC content and then they were divided into 8 groups according to natural organic matter gradient. Secondly, the experiments tested the effect of heavy metal (Cu, Zn and Ni) digestion by acids (hydrochloric acid, nitric acid and hydrofluoric acid). It was found out that heavy metals in samples with low TOC could be digested by hydrochloric acid alone. While others with high TOC requires multiple acids. Finally, after studying impact factors of aboved systems on digestions of heavy metals, optimum system (mainly the type and amount of acid) for heavy metal digestion which is based on OM gradient grading are established. Experimental results demonstrate that the established optimum digestion systems have high recovery rates (90%~110%) and detection accuracy, and their total acid consumption in 2~19 mL which are lower than the national standard digestion method, can be used for the detection of heavy metals in rivers. In summary, the optimal digestion system based on organic gradient grading is more environmentally friendly and convenient. However, limited by experimental conditions and samples, this paper only studied four digestion systems for Cu, Zn and Ni. Therefore, the proposed differential digestion method for heavy metals based on organic matter gradients has still some limitations, and need are further studied.

Acknowledgment
This study was supported by Natural Science Foundation of Zhejiang Province (No. LGF18E090009).

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