Magnetic solid-phase extraction based on multi-walled carbon nanotubes combined ferroferric oxide nanoparticles for the determination of five heavy metal ions in water samples by inductively coupled plasma mass spectrometry

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ABSTRACT

An excellent magnetic multi-walled carbon nanotubes (MMWCNT) containing carboxyl material modified with ferroferric oxide (Fe3O4) nanoparticles was synthesized as the adsorbent for magnetic solid-phase extraction (MSPE) of five heavy metal ions (Pb2+, Cu2+, Co2+, Cd2+, Cr4+) in water samples followed by on-line inductively coupled plasma mass spectrometry (ICP-MS) detection. The characteristics of the adsorbent were analyzed using Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and vibrating sample magnetometer (VSM). Some factors affecting extraction efficiency including pH of sample solution, the amount of adsorbent, extraction method and time, concentration and volume of desorption solvent, desorption time and evaluation of coexisting ions were optimized. Under the optimum conditions, good linearity (r ≥ 0.9951) was obtained within the range of 0.1–50.0 ng·mL−1. The limits of detection (LODs) and limits of quantification (LOQs) were 4.0–25.0 ng·L−1 and 15.0–80.0 ng·L−1, respectively. And satisfactory recoveries of five heavy metal ions ranged from 81.11% to 105.53% were acquired, and the relative standard deviations (RSDs) were no more than 6.05%. The MMWCNT synthesized had strong adsorption force for the five investigated heavy metal ions, respectively. Hence, the proposed method was so suitable and sensitive that it can be applied to the determination of trace analysis of heavy metals in water samples.

Key words: heavy metal ions, inductively coupled plasma mass spectrometry, magnetic multi-walled carbon nanotubes, magnetic solid-phase extraction, water samples

HIGHLIGHTS

• A novel material of Fe3O4 nanoparticles modified multi-walled carbon nanotubes was synthesized.
• An efficient, rapid and simple method for the determination of five heavy metal ions in different water samples by magnetic solid phase extraction was developed.
• This results in the method validation showed good linearity, low limit of detection and satisfactory recovery.
INTRODUCTION

Heavy metal ions that are released into the ecological environment mainly come from the wastewater of chemical factories, which is mainly produced by the processes of battery production, metallurgy and plastics. The discharge of wastewater is a very common environmental problem which can seriously threaten human health (Vilardi et al. 2018). Heavy metal ions, such as Pb$^{2+}$, Cu$^{2+}$, Co$^{2+}$, Cd$^{2+}$ and Cr$^{4+}$ are well-known as water pollutants due to their toxicity, non-degradability, and the long biological half-lives. Therefore, it is critical to detect the presence of these heavy metals in water. It has been reported that trace heavy metals were determined in environmental and biological samples using inductively coupled plasma optical emission spectrometry (ICP-OES) (Faraji et al. 2010), electrothermal atomic adsorption spectrometry (ETAAS) (Burguera & Burguera 2007), flame atomic absorption spectrometry (FAAS) (Zhao et al. 2009). Compared with other methods, inductively coupled plasma mass spectrometry (ICP-MS) was considered one of the most advisable techniques for trace analysis because of its accuracy, multi-elemental determination and low limit of detection (Su et al. 2014).

However, interferences from complex matrices and mass spectrometry have an influence on the determination of actual samples by ICP-MS. Hence, it is important to select a suitable pre-treatment method for enhancing the sensitivity on the determination of trace metals. Currently, many pre-treatments (Yang et al. 2013), including ion exchange, membrane separation, reverse osmosis, nanofiltration and adsorption, were generally applied to the determination of actual heavy metals. Among all the proposed techniques, the solid-phase extraction (SPE) using solid as the adsorbent was widely used to extract heavy metals from water (Mosavi et al. 2018).

It is well known that the pre-treatment of SPE is commonly applied to the extraction and separation of target analytes in food, biological and environmental samples. However, the non-selectivity of adsorbent in the traditional SPE method led to inaccurate quantitation of target analytes. So some additional instruments were required for analysis, which caused time and cost consuming (Ji et al. 2017). Currently, magnetic solid-phase extraction (MSPE), a highly selective extraction method, could simplify the sample preparation steps (Wang et al. 2017). In the process of MSPE, a kind of magnetic adsorbent with high affinity for analytes was added to sample solution, and then the sample matrix and adsorbent were quickly separated
by a magnet. Generally, the magnetic materials used widely in MSPE were Fe$_3$O$_4$ nanoparticles with surface modification to improve the extraction efficiency (Zhao et al. 2013). According to previous study, the binding force between the Fe$_3$O$_4$ nanoparticles and carbon nanotubes was strong enough to resist the applied mechanical energy. Hence, this method was not only extremely convenient to separate target analytes, but also had the advantage of increasing the extraction efficiency with a sharp augmentation in contact between the adsorbent and analytes (Zhao et al. 2013). In this experiment, MSPE was chosen to be widely used in various samples, especially the sample preparation technology of water samples.

Carbon nanotubes (CNTs) have received extensive multidisciplinary study because of their unique physical properties and many potential applications (Elsehly et al. 2016). The CNTs were divided into single-walled (SWCNTs) and multi-walled (MWCNTs) depending on the number of layers constituting them (Liang et al. 2014). Compared with SWCNTs, MWCNTs have shown excellent properties, including large surface area, structural characteristics and thermal stability (González-Curbelo et al. 2013). In order to improve the special adsorption capacity, the surface of CNTs was frequently functionalized by modifying different functional groups, such as –OH, –NH$_2$ and –COOH. Due to the specific complexation between metal ions and hydrophilic functional groups on the surface of MWCNTs, it was more suitable for the adsorption of heavy metals (Laforé et al. 2012; Herrero-Latorre et al. 2018). In short, considering the existence of heavy metal ions in the acidic solution, MWCNTs with carboxyl groups were selected for this study.

The aim of the present study was to develop a novel and sensitive analytical method for rapid determination of five heavy metal ions in different environmental water samples. In this study, a novel material was successfully synthesized and characterized as a suitable MSPE adsorbent. Meanwhile, some factors (including pH of sample solution, the amount of adsorbent, extraction method and time, concentration and volume of desorption solvent, desorption time and evaluation of coexisting ions) that affected the extraction efficiency of MSPE were investigated and optimized. The method was validated and used for determination of five heavy metal ions that persisted in water samples by ICP-MS.

**MATERIALS AND METHODS**

**Standards and materials**

Individual stock solutions (1 mg·mL$^{-1}$) of Cr (II), Co (II), Cu (II), Cd (II), Pb (II) were bought from National Nonferrous Metals, Electronic Materials Analysis, Testing Center GB (Beijing) Inspection and Certification Co., Ltd. The standard solution was diluted to 10 μg·mL$^{-1}$ and stored in a refrigerator at 4 °C until use. Nitric acid (HNO$_3$, assay ≥ 65%) was GR grade and acquired from Sinopharm Chemistry Reagent Co., Ltd., China (Shanghai, China). Sodium hydroxide, ammonium iron (II) sulfate [(NH$_4$)$_2$Fe(SO$_4$)$_2$·6H$_2$O] were purchased from Hengxing Chemical Reagent Factory (Tianjin, China). Carboxyl group functionalized multi-walled carbon nanotubes (MWCNTs–COOH, od of 8–15 nm, length of 50 μm) were obtained from Chinese Academy of Sciences Chengdu Organic Chemistry Co., Ltd (Chengdu, China). Ultrapure water was supplied by Hangzhou Wahaha Foods Co., Ltd (Hangzhou, China). All the reagents were of analytical grade unless otherwise specified.

**Apparatus**

The determination of heavy metal ions was performed using an Agilent 7800 inductively coupled plasma mass spectrometry (Agilent Technologies, USA). The operating parameters were set by the manufacturer and the operating conditions for ICP-MS were listed in Table 1. The spectograms (400–4,000 cm$^{-1}$) were recorded on a Bruker IFS-66 Fourier transform infrared spectrometer (Bruker, Germany). The morphology of adsorbent was described by the Scanning electron microscope. And the magnetization measurements were performed on an MPMS (SQUID) Vibrating sample magnetometer (Quantum Design, USA). A strong magnet (5 cm × 4 cm × 3 cm, 1.4 T) was used for magnetic separation.

**Sample collection and preparation**

In this experiment, five kinds of environmental water samples were selected to determine the contents of the five investigated heavy metal ions. Tap water was collected from the laboratory of Shenyang Pharmaceutical University. Purified water was obtained by filtering tap water through a brand water purifier. The farmland water came from a farmland of Xinmin. Mineral water was purchased from a supermarket in Shenyang. Rain water was collected from a tetrafluoroethylene bottle. These water samples were filtered through a 0.45 μm microporous membrane (Branch Billion Lung, Tianjin) and acidified to pH of 2 with concentrated HNO$_3$, and then kept sealed at 4 °C (Mosavi et al. 2018). The value of pH was adjusted to 6 with 5% (v/v) HNO$_3$ and 10% (v/v) NH$_3$·H$_2$O prior to extraction.
Synthesis of MMWCNT

The MMWCNT was synthesized via the chemical co-precipitation method. Under alkaline conditions, the generated Fe₃O₄ nanoparticles were covered on the surface of MWCNTs-COOH through electrostatic attraction (Zhang & Shi 2012). The preparation of MMWCNT was similar to the previously reported literatures with partial modification (Fazelirad et al. 2015; Zhao et al. 2018). Firstly, 4.18 g of NH₄Fe(SO₄)₂·12H₂O and 1.70 g of (NH₄)₂Fe(SO₄)₂·6H₂O were added to a three-necked round-bottom flask and were fully dissolved in 200 mL of ultrapure water under a water bath at 50 °C. Then, 1.0 g of MWCNTs-COOH was added to the mixed solution. The whole reaction process was carried out under the protection of N₂. After that, the pH of the solution reached 11 after adding sodium hydroxide solution, and the mixed solution was stirred at 50 °C for 30 min. Thereafter, the MMWCNT was separated from the mixed solution with a permanent magnet (Jiang et al. 2016), and washed three times with deionized water and ethanol, respectively. Finally, the MMWCNT was dried at 60 °C for 12 h and then ground for further use.

Extraction procedure

30 mg of MMWCNT powder were added to a centrifuge tube containing a 20 mL water sample. The suspension, whose pH was adjusted to 6, was vortexed for 10 min so the samples could be thoroughly mixed with the magnetic materials. The mixture was adsorbed by a permanent magnet, and then the supernatant was discarded. Afterwards, 10 mL 5% (v/v) HNO₃ eluent was added into the tube and vortexed for 6 min to elute the target heavy metal ions. The desorption solution, which was collected and filtered in the 10 mL centrifuge tube, was directly analyzed and detected with ICP-MS. The used MMWCNT materials were washed with 2% (v/v) HNO₃, ultrapure water and ethyl alcohol absolute several times, respectively. Finally, the nanoparticles were dried for recycle use.

RESULTS AND DISCUSSION

Characterization of MMWCNT

The modification of MMWCNT was identified using FT-IR spectra in Figure 1(a). Compared with MWCNTs-COOH, it can be clearly seen that an absorption peak at 585.1 cm⁻¹ appeared on the spectra of MMWCNT. The absorption peak that was attributed to the stretching vibration of Fe-O indicated that Fe₃O₄ nanoparticles were successfully embedded in MWCNTs-COOH. Additionally, the strong absorption peak at 5,421.7 cm⁻¹ was associated with the stretching vibration of –OH bonds, and the peaks located at 1,631.5 and 1,394.6 cm⁻¹ corresponded to the stretching vibration of C = O and –CH bonds.

The technology of SEM was employed to study the morphology of MWCNTs-COOH and MMWCNT, and the images are shown in Figure 1(b) and 1(c), respectively. From the two images, it was shown that the Fe₃O₄ nanoparticles were uniformly distributed on the surface of MWCNTs-COOH. Therefore, the iron oxides have been successfully combined with MWCNTs-COOH, which simultaneously ensured high adsorption ability of MMWCNT.

VSM was commonly applied to evaluate the magnetic property of magnetic nanoparticles. The magnetization curve (Figure 1(d)) was acquired by analyzing MMWCNT, and it clearly indicated that the hysteresis loop of MMWCNT was the
The saturation magnetization was 25.7 emu·g⁻¹. Besides, there was no magnetization in the absence of a magnetic field, which indicated that the MMWCNT had superparamagnetic properties. Furthermore, as shown in Figure 1(e), the MMWCNT could be evenly distributed in the sample solution and the MMWCNT materials could be completely and rapidly separated from the sample solution under an external magnetic field. Thus, it manifested that the MMWCNT had good magnetic properties and uniformity, which was effectively applied to the determination of actual samples.

Figure 1 | Results of MMWCNT characterization. FT-IR spectra of MWCNT-COOH and MMWCNT (a), SEM image of MWCNT-COOH (b), SEM image of MMWCNT (c), magnetization curve of MMWCNT (d), magnetic response of MMWCNT to external magnetic field (e).
Optimization of MSPE procedure

The process of magnetic solid-phase extraction plays a crucial role in the whole experiment. To get the optimal conditions for excellent extraction efficiency, the main factors of the MSPE procedure were optimized, respectively, such as pH of sample solution, the amount of adsorbent, extraction method and time, concentration and volume of desorption solvent, desorption time and evaluation of coexisting ions.

Effect of pH

The pH of the sample solution can immensely affect the capability of MMWCNT to adsorb heavy metal ions. Considering the existence of heavy metal ions in the acidic solution, MMWCNT with carboxyl groups were selected for this study. Due to the specific complexation between metal ions and hydrophilic functional groups on the surface of MMWCNT, it is more suitable for the adsorption of heavy metals. The carboxyl groups on the surface of MMWCNT are almost dissociable groups, which can change the existing forms of the target analytes, so the pH value will significantly affect the whole MSPE process. Therefore, an appropriate pH can not only improve the extraction recovery, but also depress the obstruction of coexisting ions.

In this experiment, the pH on the extraction recovery of the heavy metal ions at 2, 4, 6, 8, 10 and 12 was studied, and the results are shown in Figure 2(a). Obviously, satisfactory recoveries of heavy metal ions were obtained when the pH of the sample solution was 6, and in this condition, the MMWCNT had the strongest adsorption with heavy metal ions. With the strong acid conditions, the MMWCNT hardly absorbed heavy metal ions, which caused low extraction efficiency. This may be caused by the dissolution or oxidation of ferromagnetic materials at very low pH, which reduces the adsorption efficiency of MSPE (Yuan et al. 2013). While the pH increased from 8 to 12, the recoveries of heavy metal ions also decreased gradually, which

Figure 2 | Effect of sample solution pH (a), effect of the amount of adsorbent (b), effect of the extraction time (c) and effects of the concentration of desorption solvent on the extraction efficiency of the analytes in the process of MSPE (d).

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might result from the hydrolysis of heavy metal ions in alkaline solution (Taghizadeh et al. 2014). Hence, the sample solution with a pH of 6 was selected to guarantee satisfactory extraction efficiency of five heavy metal ions for further experiment.

**Effect of the amount of adsorbent**

The amount of adsorbent is one of the most important parameters, which has a great impact on extraction efficiency. In this experiment, the extraction efficiency was investigated when the amount of adsorbent was 10, 20, 30, 40, 50 and 60 mg. As shown in Figure 2(b), it was clearly seen when the amount of adsorbent was 15–30 mg, the extraction recovery of five heavy metal ions increased continuously. And then, there was no apparent increase with the increase of adsorbent amount. Thus, 30 mg MMWCNT was selected as the optimal amount of adsorbent for further studies.

**Effects of extraction method and time**

A suitable extraction method can extremely affect the extraction efficiency. In this experiment, extraction methods including ultrasound and vortex were studied. The results showed that the extraction efficiency of vortex was much higher than that of ultrasound. It might be explained by the fact that vortex can increase the contact area between MMWCNT and water samples. Hence, this experiment finally chose the method of vortex for extraction.

Appropriate extraction time ensured the adequate reaction between the target analytes and MMWCNT. In this work, the effect of extraction time (from 1 to 10 min) was investigated. As shown in Figure 2(c), the extraction recovery increased observably with vortex time from 1 to 6 min. When the vortex time exceeded 6 min, the extraction recovery hardly changed, showing that 6 min of vortex time was optimal. Therefore, the vortex time of this experiment was 6 min.

**Effects of the concentration of desorption solvent**

The selection of elution solvent plays an important role in resolving the target heavy metal ions more quickly and completely. In this study, the recovery of three different concentrations (2%HNO₃, 5%HNO₃, 10%HNO₃) of the elution solvent was investigated in the same volume. The results (Figure 2(d)) indicated that the elution recoveries of Cr²⁺, Co²⁺ and Cu²⁺ were lowest when using 2%HNO₃, while using 5%HNO₃ and 10%HNO₃, the elution recoveries of five heavy metal ions were satisfactory.

**Effects of the volume of desorption solvent**

Furthermore, the elution efficiency was investigated when the volume of 5%HNO₃ was 4, 6, 8, 10, 12 and 15 mL. As shown in Figure 3(a), the results illustrated that the elution recovery increased continuously with 4–10 mL of 5%HNO₃. When the elution volume was more than 10 mL, the recoveries of five heavy metal ions no longer increased with the increase of 5%HNO₃ volume, indicating 10 mL of 5%HNO₃ was sufficient for eluting five heavy metal ions. Thus, 10 mL of 5%HNO₃ was selected as the elution solvent in the process of MSPE to reduce the use of nitric acid.

![Figure 3](http://iwaponline.com/wst/article-pdf/84/6/1417/942144/wst084061417.pdf)

**Figure 3** | Effects of the volume of desorption solvent on the extraction efficiency of the analytes in the process of MSPE (a), effect of desorption time (b) on the extraction efficiency of the analytes in the process of MSPE.
Effect of desorption time

An appropriate desorption time has a critical role in the elution of the target heavy metal ions, which can improve the extraction efficiency. In this work, desorption times were tested in the range of 1–10 min with the same desorption solvent (Figure 3(b)). The results showed that the extraction recoveries of five heavy metal ions were significantly improved with desorption time increasing from 1 to 6 min. The extraction recovery was almost constant when desorption time exceeded 6 min. Furthermore, a simple t-test of desorption time in the two periods of 6–8 and 8–10 min were tested. The results of the t-test showed $p > 0.05$, so it can be concluded that there were no significant differences between 6, 8, and 10 min. Therefore, 6 min was finally used as desorption time.

Effect of coexisting ions

The effects of common coexisting ions such as $K^+$, $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ on the extraction and determination of five heavy metal ions were investigated. In this study, 10 ng·mL$^{-1}$ of each target analyte and a series of coexisting ions added to ultrapure water were studied under the optimum conditions. The tolerance limit was defined as the maximum amount of coexisting ions which made the recoveries of the target analytes in the range of 85–115% (Su et al. 2014). The experimental results indicated that 10000-fold of $K^+$ and $Na^+$, 6000-fold of $Ca^{2+}$, and 3000-fold of $Mg^{2+}$ hardly affected the extraction and determination of five heavy metal ions. Thus, the developed method had good selectivity.

Adsorption capacity

One of the important factors in evaluating the performance of adsorbents is the adsorption capacity. The adsorption capacity of MMWCNT was evaluated by the way described in the literature (Roya et al. 2018). In this method, 15 mg of MMWCNT was added into a conical flask containing 50 mL of 50 μg·mL$^{-1}$ five heavy metal ions standard solution. At a constant temperature, the mixed solution was shaken at the speed of 2,000 rpm for 1 h. Then, the contents of five heavy metal ions in the supernatant were determined by ICP-MS. And then the calculation formula of the adsorbed amount of heavy metals ($q_e$) was as follows:

$$q_e = \frac{(C_0 - C_e) \times V}{W}$$

where $C_0$ and $C_e$ (mg·L$^{-1}$) represent the initial and equilibrium concentrations of heavy metal ions, respectively, $V$ (L) means the volume of heavy metal ions, and $W$ (mg) stands for the amount of adsorbent. The results showed that the maximum adsorption capacity of MMWCNT for $Pb^{2+}$ and $Cd^{2+}$ was 95 mg·g$^{-1}$, $Cu^{2+}$ and $Co^{2+}$ was 91 mg·g$^{-1}$, and 85 mg·g$^{-1}$ of $Cr^{4+}$.

Method validation

Under the optimized conditions, linearity, LOD and LOQ, precision and recovery of the proposed method for extraction and determination of the target analytes were validated and the results are presented in Tables 2 and 3, respectively. In this experiment, distilled water was used as the blank solvent. The linearity of the method was investigated by using a series of gradient standard solutions of five heavy metal ions with the range of 0.1–50.0 ng·mL$^{-1}$. The LOD and LOQ were calculated with 3 times and 10 times standard deviation of blank signal intensity. The precision of the instrument was determined by analyzing the standard solutions of five heavy metal ions 11 times. To evaluate the recovery of the method, water samples were spiked at three concentration levels to compare the contents of the target analytes.

| Analytes | Linear range (ng·mL$^{-1}$) | $r$ | LOD (ng·L$^{-1}$) | LOQ (ng·L$^{-1}$) | Precision RSD (%) |
|----------|-----------------------------|-----|-----------------|------------------|------------------|
| Pb$^{2+}$ | 0.1–50.0                    | 0.9999 | 11.0           | 40.0             | 1.5              |
| Cu$^{2+}$ | 0.1–50.0                    | 0.9998 | 9.0            | 30.0             | 1.9              |
| Co$^{2+}$ | 0.1–50.0                    | 0.9998 | 25.0           | 80.0             | 1.3              |
| Cd$^{2+}$ | 0.1–50.0                    | 0.9999 | 4.0            | 15.0             | 1.4              |
| Cr$^{3+}$ | 0.1–50.0                    | 0.9951 | 16.0           | 50.0             | 1.5              |
The calibration curves of target analytes had good linear relationship in the range of 0.1–50.0 ng·mL⁻¹ with all correlation coefficients (r) higher than 0.9951. The LODs and LOQs of the five target analytes ranged from 4.0–25.0 ng·L⁻¹ to 15.0–80.0 ng·L⁻¹, respectively. The precision of the instrument expressed as RSD ranged from 1.3% to 1.9%. The spiking-recovery of five target metals in different water samples was in the range of 81.11%–105.53%, and the RSD was less than 6.05%. The evaluation results were in accordance with the European Union guidelines SANCO/12495/2011, the spiking-recovery should be in the range of 70–120% with RSD less or equal 20%. Therefore, the results of the method validation indicated that this sensitive and efficient method was suitable for the determination of five heavy metal ions in water samples.

### Application in actual water samples

Under the optimized conditions, the developed MSPE-ICP-MS method was successfully used in the determination of five heavy metal ions in five kinds of water samples. The results are listed in Table 4. It can be clearly seen that all five heavy metal ions were detected in tap water, rain water and farmland water, less Pb²⁺, Cu²⁺ and Co²⁺ were detected in purified water, while no heavy metal ions were detected in the mineral water.

### Comparison of this method with others

This method was compared with other methods reported in the literatures (Zhao et al. 2009; Taghizadeh et al. 2014; Huang et al. 2015; Roya et al. 2018; Chen et al. 2019) for determining the contents of metal ions to evaluate its reliability and applicability. It is obviously seen from Table 5 that this developed method, compared with SPE-AFS, SPE-FAAS and Dmspe-ICP-

### Table 3 | Spiked recoveries of five heavy metal ions in different water samples

| Analytes      | Spiked (ng·mL⁻¹) | Recovery ± RSD (%) (n = 3) |
|---------------|-----------------|-----------------------------|
|               | Tap water       | Purified water              | Mineral water     | Rain water       | Farmland water |
| Pb²⁺          | 1.0             | 91.40 ± 2.63                | 100.50 ± 2.99     | 97.97 ± 3.42     | 101.73 ± 1.92  | 101.07 ± 1.27  |
|               | 5.0             | 95.53 ± 1.55                | 96.13 ± 1.62      | 95.04 ± 1.59     | 87.02 ± 0.89   | 92.24 ± 1.84   |
|               | 20.0            | 94.19 ± 4.86                | 94.30 ± 0.44      | 91.22 ± 0.61     | 92.38 ± 0.73   | 96.77 ± 0.59   |
| Cu²⁺          | 1.0             | 93.63 ± 4.45                | 97.03 ± 4.73      | 91.17 ± 1.89     | 92.03 ± 2.22   | 85.00 ± 0.73   |
|               | 5.0             | 93.40 ± 1.99                | 90.58 ± 1.61      | 95.05 ± 1.64     | 85.58 ± 2.00   | 97.63 ± 1.95   |
|               | 20.0            | 92.38 ± 2.00                | 95.69 ± 1.59      | 86.49 ± 0.32     | 85.17 ± 0.27   | 85.71 ± 0.80   |
| Co²⁺          | 1.0             | 89.20 ± 2.32                | 105.53 ± 5.88     | 92.15 ± 5.60     | 85.23 ± 6.05   | 88.90 ± 1.30   |
|               | 5.0             | 104.95 ± 1.96               | 94.25 ± 1.59      | 92.58 ± 1.66     | 85.06 ± 1.22   | 100.06 ± 0.71  |
|               | 20.0            | 97.75 ± 0.36                | 81.11 ± 3.27      | 91.43 ± 1.18     | 92.16 ± 1.96   | 98.48 ± 0.27   |
| Cd²⁺          | 1.0             | 91.40 ± 1.70                | 96.97 ± 5.51      | 96.70 ± 5.26     | 87.00 ± 2.10   | 86.17 ± 1.91   |
|               | 5.0             | 92.83 ± 1.83                | 90.25 ± 0.94      | 88.28 ± 1.67     | 87.15 ± 0.94   | 90.59 ± 1.78   |
|               | 20.0            | 96.08 ± 1.15                | 96.43 ± 1.40      | 94.22 ± 3.88     | 93.65 ± 0.17   | 94.40 ± 0.06   |
| Cr²⁺          | 1.0             | 93.00 ± 4.30                | 98.40 ± 2.50      | 98.40 ± 2.50     | 87.20 ± 1.65   | 86.70 ± 2.66   |
|               | 5.0             | 97.42 ± 1.99                | 92.73 ± 1.27      | 92.73 ± 1.27     | 93.01 ± 0.94   | 90.78 ± 1.68   |
|               | 20.0            | 89.72 ± 1.27                | 93.57 ± 1.51      | 93.57 ± 1.51     | 93.47 ± 0.28   | 92.21 ± 1.73   |

| Note: – not detected |
MS, can simultaneously determine the contents of multiple metal ions, and also has the advantage of high adsorption capacity for metal ions. Compared with SPE-FAAS and Microcolumn preconcentration-FAAS, not only does this method have high adsorption capacity, but this method also has lower LOD. In summary, due to its simplicity, high extraction efficiency and satisfactory recovery, this proposed method can be applied to the detection of heavy metal ions residues.

**CONCLUSIONS**

In the present study, the magnetic solid-phase extraction method based on the materials of MMWCNT for the determination of Pb²⁺, Cu²⁺, Co²⁺, Cd²⁺, and Cr⁴⁺ in water samples by the combination of ICP-MS has been assessed. Based on the optimal conditions, the method exhibited low LODs, good precision and satisfactory recovery. And this method has been successfully applied to the determination of five trace heavy metal ions in different water samples. Moreover, the adsorbent MMWCNT can be reused up to three times, which not only reduces the costs of experiments, but also meets the requirements of green chemistry. In short, the procedure provides great application prospects in the analysis of metal ions residues in different matrices.

**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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**Table 5** Comparison of the developed method with other methods for the determination of metal ions

| Method                  | Element                | Adsorption capacity (mg·g⁻¹) | LOD (ng·L⁻¹) | RSD (%) | Reference |
|-------------------------|------------------------|-----------------------------|--------------|---------|-----------|
| SPE-AFS                 | As                     | –                           | 2            | 5.3     | 21        |
| SPE-FAASb               | Pb                     | 80.81                       | –            | –       | 22        |
| Dmsep-ICP-MSc           | Lanthanides            | 25.9–32.7                   | 0.01–1.2     | 2.5–6.3 | 23        |
| SPE-FAAS                | Cu, Cd, Pb, Zn, Ni, Co | 7.3–14.2                    | 300–600      | <5      | 24        |
| Microcolumn preconcentration-FAAS | Cu, Zn, Mn, Pb | –                           | 280–1,000    | 2.6–4.6 | 25        |
| MSPE-ICP-MS             | Cu, Cd, Pb, Cr, Co     | 85–95                       | 4–25         | 1.3–1.9 | This work |

aSolid-phase extraction-atomic fluorescence spectrometry.
bSolid-phase extraction-flame atomic absorption spectrometry.
cDispersive micro-solid phase extraction-inductively coupled plasma mass spectrometry.
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First received 16 January 2021; accepted in revised form 31 July 2021. Available online 16 August 2021