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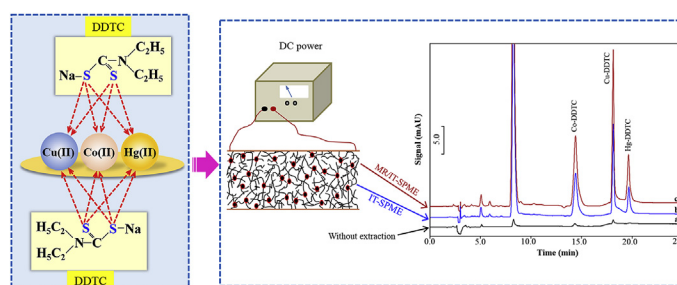
Magnetism-reinforced in-tube solid phase microextraction for the online determination of trace heavy metal ions in complex samples

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HIGHLIGHTS

- MR/IT-SPME was firstly proposed to extract heavy metal ions.
- The exertion of magnetic field could improve the extraction efficiencies obviously.
- Extraction parameters were optimized in detail.
- The applicability of the current online MR/IT-SPME-HPLC-DAD method was demonstrated.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, a convenient, online couplable, sensitive and environmentally friendly sample pre-treatment method, namely, magnetism-reinforced in-tube solid phase microextraction (MR/IT-SPME) was proposed to effectively enrich heavy metal ions (HMIs). Monolithic capillary microextraction column embedded modified Fe_3O_4 magnetic nanoparticles (MCEN) was conveniently synthesized and employed as the microextraction column of MR/IT-SPME. Subsequently, the MCEN was put into a magnetic coil which was utilized to exert variable magnetic field during extraction procedure. Three HMIs, including Cu(II), Co(II) and Hg(II), were selected as studied ions and reacted with chelating agent sodium diethyldithiocarbamate tetrahydrate to form metallic coordination compounds. The complexes were infused to the MCEN to perform the MR/IT-SPME extraction and then online determined by high-performance liquid chromatography equipped with diode array detection (HPLC-DAD). A series of key parameters affecting the extraction performance were investigated in detail. Results revealed that the exertion of magnetic field in adsorption and desorption steps favored the adsorption and release of the coordination compounds, with the extraction efficiencies enhanced from 47–65% to 67–89%. Finally, the developed online MR/IT-SPME-HPLC-DAD approach was successfully applied to determine studied HMIs in environmental water and seafood samples. The confirmatory experiments further evidenced the reliability and feasibility of the introduced approach for the analysis of trace HMIs in complex samples.

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1. Introduction

Due to the intensive industrial activities and improper disposal of wastes, an increasing number of heavy metal ions (HMIs) have been released into environment. Many of HMIs show good stability, strong bioaccumulation and high toxicity. Once heavy metal pollutant occurs, it will bring fatal threat to humans and other organisms [1]. Thus, developing robust methods to monitor HMIs concentration levels is very necessary.

So far, atomic absorption spectrometry (AAS) [2,3], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [4,5], inductively coupled plasma-mass spectrometry (ICP-MS) [6–8] and electrochemical method [9] are the most common techniques to analyze HMIs. In addition to above-mentioned methods, high-performance liquid chromatography (HPLC) coupled to UV absorbance detection has also achieved rapid development in the analysis of HMIs due to the advantages of high separation efficiency, flexibility, simplicity and cost-effectiveness [10]. When using HPLC-UV to analyze HMIs, chelating agent should be firstly used to coordinate with HMIs to meet the requirement of chromatographic separation and make the metal ions UV sensitive. Besides, considering the complexity of the sample matrix and the trace levels of HMIs, suitable sample pretreatment should be performed before chromatographic analysis. Currently, a few of methods such as liquid-liquid extraction (LLE) [11], single-drop microextraction (SDME) [12], dispersive liquid-liquid microextraction (DLLME) [13], solid-phase extraction (SPE) [14–19], solid-phase microextraction (SPME) [20] and cloud-point extraction (CPE) [21] have been developed and successfully applied to extract HMIs from multifarious samples. However, the above-mentioned methods are operated offline and can't be online coupled to chromatographic system to realize the automated extraction and analysis.

In-tube solid-phase microextraction (IT-SPME) is an important branch of SPME. It not only inherits the advantages of SPME including simplicity, environment-friendliness, but also displays other attractive merits such as easy automation and online coupling with HPLC [22]. In the past decades, IT-SPME has been widely applied to extract various organic compounds [23–25], but rarely used to enrich HMIs. Furthermore, the reported studies indicate that the unsatisfactory extraction efficiency of IT-SPME restricts its application. To solve the drawback, Campins-Falcó and co-workers proposed magnetic-IT-SPME method based on the magnetic microfluidic principle and the diamagnetism of analytes [26,27]. In their works, $\text{Fe}_3\text{O}_4/\text{SiO}_2$ nanoparticles were immobilized in the inner surface of silica capillary column to form a magnetic extraction phase. After that, the capillary column was wrapped with a magnetic coil. During the adsorption and desorption procedure, different directions of magnetic fields were exerted. Results well indicated that the magnetic force could improve the extraction efficiencies of target organic analytes obviously. However, in their research, open-tubular capillary column (OTCC) was used to extract analytes. For OTCC, the adsorbent utilized to extract target analytes is limited, resulting in low extraction capacity of magnetic-IT-SPME. To find a more effective solution, magnetism-enhanced monolith-based IT-SPME (ME-MB/IT-SPME) was developed in our group. The ME-MB/IT-SPME combines the magnetic microfluidic principles, diamagnetism of studied analytes and the unique merits of monoliths [28]. Results have well evidenced that the ME-MB/IT-SPME was an effective way to overcome the drawbacks of conventional IT-SPME. It has been online coupled to HPLC equipped with diode array detection (HPLC-DAD) to analyze steroid hormones [28], triazines [29] and organic UV filters [30] in environmental waters successfully.

Based on our previous studies [28–30], in this work, we tried to develop a novel magnetism-reinforced IT-SPME (MR/IT-SPME)

method for the efficient enrichment of HMIs. To meet the requirement of chromatographic separation and UV detection, HMIs including Co(II), Cu(II) and Hg(II) were reacted with sodium diethyldithiocarbamate trihydrate (DDTC) to form metallic coordination compounds. According to the molecular structures of coordination compounds, a new monolithic capillary microextraction column embedded Fe_3O_4 magnetic nanoparticles (MCEN) was synthesized using 4-vinylphenylboronic acid (VA) and ethylene dimethacrylate (ED) as functional monomer and cross-linker, respectively. After that, the MCEN was wrapped with a magnetic coil which allowed the application of variable magnetic fields during the adsorption and desorption steps. Under the optimized conditions, the MR/IT-SPME was online combined with HPLC-DAD to quantify trace Cu(II), Co(II), Hg(II) in environmental waters and seafood samples. Results well evidence that the implementation of magnetic fields can enhance the extraction efficiency of studied metal ions obviously. The proposed online MR/IT-SPME-HPLC-DAD method is automatic and robust in the monitoring of trace HMIs.

2. Experimental

2.1. Chemicals

VA (98%) and azobisisobutyronitrile (AIBN) (98%) were supplied by Shanghai Dibai Chemical Technology Co., Ltd. (Shanghai, China) and Shanghai Chemical Co. (Shanghai, China), respectively. ED (97%), and 3-(trimethoxysilyl) propylmethacrylate (γ -MAPS) (95%) were bought from TCI (Shanghai) Development Co., Ltd (Shanghai, China). Nitric acid (HNO_3) (65–68%) of guarantee reagent grade, N,N-dimethylformamide (DMF) (99.5%), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (98%) and tetraethylorthosilicate (TEOS) (98%) of analytical reagent grade were purchased from Xilong Scientific Co., Ltd (Guangdong, China). *p*-Xylene ($\geq 98.5\%$) was obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Acetonitrile (ACN) and methanol were HPLC-grade and supplied by Tedia Company Inc. (Fairfield, USA). Ultrapure water prepared from a Milli-Q water purification system (Merck Millipore, Germany) was used throughout the study. Fused silica capillary (320 μm i.d.) used as the mold to synthesize MCEN was got from Ruifeng Instrumental Co., Ltd (Hebei, China).

The standard stock solutions of Co(II), Cu(II) and Hg(II) (the concentrations were all 1000 mg/L) were supplied by National Research Center for Standard Substances (Beijing, China). The mixed solution containing 50, 50, 100 mg/L of Co(II), Cu(II) and Hg(II), respectively, was prepared by diluting individual stock solutions in ultrapure water. The chelating agent DDTC ($\geq 98\%$) was purchased from ANPEL laboratory technologies Co., Ltd. (Shanghai, China) and its working solution at a concentration of 0.02 mol/L was prepared in methanol. All solutions were stored at 4 °C and diluted with ultrapure water to give the required concentration.

2.2. Apparatus and analytical conditions

The established analytical system for Co(II), Cu(II) and Hg(II) consisted of two parts. The pretreatment part included a Rheodyne model 7725i high-pressure six-port valve (V 1) (Cotati, CA, USA) and a TPR-6405D DC power supply (Long Wei, Guangzhou, China). The delivery of sample and desorption solution was realized with two P230 II high pressure pumps (pump A and pump B) (Elite, Dalian, China). In the chromatographic separation part, the HPLC analysis was performed on the Agilent 1260 LC chromatographic system (USA) equipped with a quarter pump (pump C) (1260 Quat Pump) and a diode array detector (1260-DAD). Another Rheodyne model 7725i high-pressure six-port valve (V 2) equipped with a 200 μL sample loop was used as injection valve (Cotati, CA, USA). All

separation was carried out on a Hypersil BDS C18 column (5 μm particle size, 250 mm \times 4.6 mm i.d.) (Thermo Fisher Scientific, USA). Methanol and ultrapure water were used as mobile phase A and B, respectively. The gradient was as follows: 0–13.0 min, 65% B –69% B; 13.0–14.0 min, 69% B –78% B and kept for 7.0 min; 21.0–22.0 min, 78% B–65% B and kept for 3.0 min. The flow rate was set at 1.0 mL/min and the detection wavelength was 270 nm.

The morphologies of MCEN were investigated using transmission electron microscopy (TEM) (JEOL 2011 microscope, Japan) and scanning electron microscopy (SEM) (Sigma ZEISS, ZEISS, Germany). Magnetic properties of three metallic coordination compounds and the MCEN were carried out on a PPMS-9 vibrating sample magnetometer (QUANTOM, USA); Oxford X-MaxN energy dispersive spectroscopy was supplied by Oxford Instruments (UK).

2.3. Synthesis of MCEN

To make the Fe_3O_4 magnetic nanoparticles combine the monolithic material stably, the Fe_3O_4 was modified with TEOS and γ -MAPS in succession to obtain $\text{Fe}_3\text{O}_4@\text{SiO}_2@\gamma$ -MAPS. The detailed modification procedure can be found in our previous study [28].

The subsequent polymerization process is shown in Fig. 1. Briefly, 120 mg VA, 180 mg ED, 680 mg *p*-xylene, 400 μL DMF and 20 mg AIBN was homogenized under the ultrasonication for 20 min. Thereafter, 25 mg $\text{Fe}_3\text{O}_4@\text{SiO}_2@\gamma$ -MAPS was added and dispersed in the solution by means of continuous ultrasonication. The above mixture was filled into a capillary column (20 cm \times 320 μm i.d.). After that, the both ends of the capillary were sealed, and then the capillary was kept in an oven at 60 $^\circ\text{C}$ for 12 h. After the polymerization, the MCEN was washed with methanol at the flow rate of 0.10 mL/min for 30 min to remove the un-reacted monomer and cross-linker.

2.4. Operation procedure of online MR/IT-SPME-HPLC-DAD system

Fig. S1 describes the operation procedure of proposed online MR/IT-SPME-HPLC-DAD system at adsorption (a), desorption (b)

and HPLC analysis (c) stages. As shown, two six-port valves (V 1 and V 2) were used and connected with one polyether ether ketone tube (18 cm \times 250 μm i.d.). The prepared MCEN wrapped with a magnetic coil was placed on V 1. The magnetic coil was connected to a DC power supply (the relationship of the magnetic field intensity (B) with DC current can be seen in our previous study [29]). The analysis of HMIs with the MR/IT-SPME-HPLC-DAD system includes three steps. The first step is the adsorption procedure (Fig. S1a). V 1 and V 2 were set at LOAD position. Pump A was turned on to carry the sample solution (4 mL) through the MCEN at the flow rate of 0.14 mL/min for adsorption of the metallic coordination compounds. At the same time, the DC power was switched on to impose an intensity of 20 Gs magnetic field with the same direction as sample solution passing through the MCEN. At this stage, the chromatographic column was conditioned by mobile phase driven by Pump C. The second step is the desorption procedure. As shown in Fig. S1b, after the adsorption, Pump A was turned off and V 1 was changed to INJECT position while V 2 was still kept at LOAD position. The intensity of the magnetic field was adjusted to 40 Gs with its polarity reversed. Methanol (0.08 mL) used as desorption solvent was driven by Pump B at a flow rate of 0.04 mL/min to release the extracted compounds from the MCEN. The eluent was subsequently transferred to the sample loop fastened on V 2. After the desorption step, Pump B and the external power were turned off. Switching V 2 to the INJECT position, the analytes were delivered into HPLC by the mobile phase for chromatographic separation and analysis (Fig. S1c). Meanwhile, V 1 was kept in INJECT position. The MCEN was washed with methanol at a flow rate of 0.10 mL/min for 10 min to avoid carry-over effects. After the recondition, the MCEN was reused in the next extraction.

2.5. Collection and preparation of real samples

Water samples were collected from Xiamen City and stored in 500 mL polyethylene bottles in darkness at 4 $^\circ\text{C}$ before use. All samples were filtrated through nylon syringe filters with 0.22 μm pore size. Subsequently, the water samples were adjusted to pH 7.0,

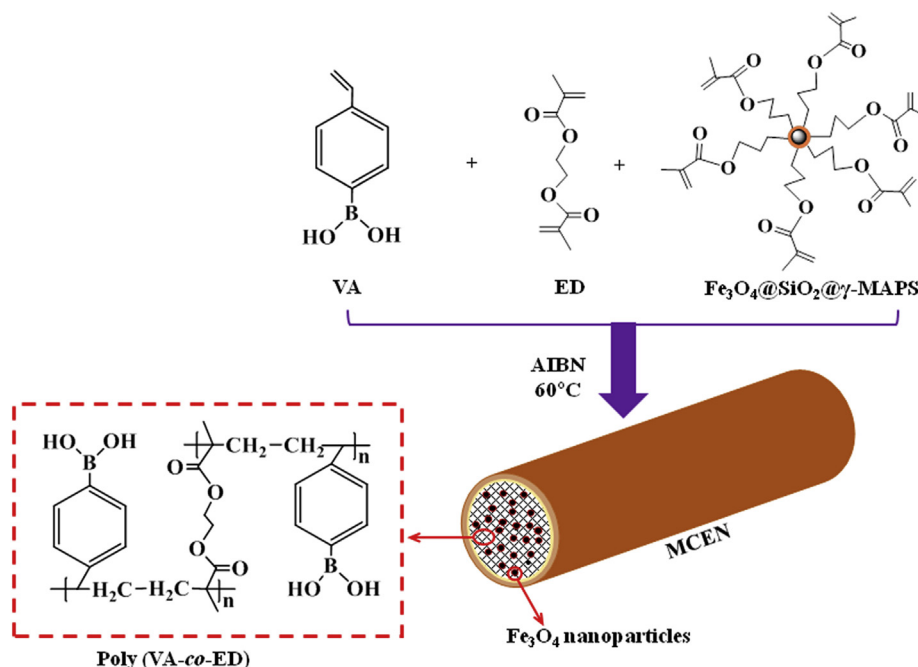


Fig. 1. The polymerization schematic of MCEN.

and then a certain amount of chelating agent (equals to 20 times of the molar concentration of studied HIMs) was added to the sample solutions. After reacting for 5 min at room temperature, the samples were analyzed with the developed MR/IT-SPME-HPLC-DAD method.

Seafood samples including fish and shrimp were bought from local market. First of all, the muscle tissue of fish and the edible part of shrimp were cut off using a plastic knife and separately put in clean plastic bags. The samples were freeze-dried at -80°C for 24 h. Next, 0.5 g dried sample was weighted into 15 mL centrifuge tube and 1.0 mL concentrated HNO_3 was added. The sample was subjected to heating digestion at 80°C for 8 h. After that, the digestion solution was evaporated to near dryness and the residue was dissolved with ultrapure water. The un-dissolved substances were filtrated through filter of $0.22\ \mu\text{m}$ pore size and the clean filtrate was diluted to 50 mL with ultrapure water. The pH of the solution was adjusted to 7.0 and the subsequent process was the same as in the case of water samples.

3. Results and discussion

3.1. Consideration and preparation of MCEN

To meet the requirement of HPLC-DAD analysis, the target Co(II), Cu(II) and Hg(II) should react with chelating agent to form metallic coordination compounds. DDTC could react with HIMs quickly at room temperature to form stable complexes, thus it was selected as chelating agent [31]. In the present study, the target Co(II), Cu(II) and Hg(II) coordinated with DDTC to form Co-DDTC, Cu-DDTC and Hg-DDTC complexes, respectively. The formed coordination compounds possess UV sensitivity, and thus meet the requirement of HPLC-DAD. In addition, the base of magnetic microfluidic principle used for the focus or trap analytes is the diamagnetism of target compounds. To evaluate the magnetic features of the complexes, the pure substances of Co-DDTC, Cu-DDTC and Hg-DDTC were prepared (the detailed synthesized procedure and the analytical results of purity can be found in the Supplementary data). The magnetic analysis results showed that the magnetic susceptibility values of Co-DDTC, Cu-DDTC and Hg-DDTC were -1.51×10^{-6} , -7.74×10^{-7} and -1.77×10^{-6} emu/(g·Oe), respectively, indicating that the MR/IT-SPME method is suitable to extract these three complexes.

Another factor should be considered in the development of MR/IT-SPME is the design and preparation of MCEN. Monoliths possess a lot of advantages such as simple synthesis, good permeability and high stability, so it is considered to be an ideal adsorbent in sample preparation [32]. Although there are many chemicals that can be utilized to synthesize monoliths, to achieve the expected extraction performance, the functional monomer should be selected according to the chemical properties of analytes. In the molecule of DDTC, there are abundant nitrogen atoms. Therefore, VA containing boronic acid groups was selected as functional monomer to prepare the MCEN. According to the principle of boronate affinity, the B–N coordination interaction between the adsorbent and metallic coordination compounds will contribute to the extraction. In addition, the quantity of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\gamma\text{-MAPS}$ in the polymerization should be considered. The preliminary experiment evidenced that the permeability of MCEN was poor if too many $\text{Fe}_3\text{O}_4@\text{SiO}_2@\gamma\text{-MAPS}$ nanoparticles were mingled into the monolith. However, the magnetic interaction sites were not enough and the magnetism-enhanced effect was unsatisfactory when a low content of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\gamma\text{-MAPS}$ nanoparticles were added to the polymerization solution. After optimization, the most favorable amount of $\text{Fe}_3\text{O}_4@\text{SiO}_2@\gamma\text{-MAPS}$ nanoparticles was 25 mg in 1.0 g polymerization solution.

Fig. S2 shows the FT-IR of the prepared MCEN. As shown, the

bands presenting at $2984\ \text{cm}^{-1}$ and $2950\ \text{cm}^{-1}$ are belonged to the CH_3 and CH_2 groups, respectively. The strong adsorption band observed at $1731\ \text{cm}^{-1}$ can be assigned to C=O stretching vibration of ED. The bands at $1610\ \text{cm}^{-1}$ and $1561\ \text{cm}^{-1}$ reveal the existence of phenyl groups. The band at $1413\ \text{cm}^{-1}$ can be attributed to the B–O vibration. These main adsorption bands in FT-IR spectrum indicate the successful polymerization of VA and ED. The EA results revealed that its carbon and hydrogen contents were 60.1% and 9.8% (w/w), respectively, which further proved the successful fabrication of MCEN.

The morphologies of MCEN were investigated by SEM. It can be seen from Fig. S3a that the monolith is tightly bonded to the inner wall of capillary. Besides, the uniform globular and porous structure of monolith can be clearly observed. These features ensure the good permeability and high mechanical stability of MCEN. The TEM image (Fig. S3b) shows that the Fe_3O_4 nanoparticles are homogeneously dispersed and embedded in the monolith. The Fe content measured by EDS was 0.51% (w/w). The EDS result further verifies the presence of Fe_3O_4 nanoparticles in the monolith.

The Fe_3O_4 nanoparticles embedded in the monolith plays an important role in the improvement of extraction efficiency. Thus, the magnetization properties of these nanoparticles were investigated by measuring their magnetization curves at both room temperature (300 K) and low temperature (5 K). The result shown in Fig. S3c demonstrates that the magnetization curve at room temperature exhibits as an s-shaped curve, with no obvious hysteresis and remanence. The magnetization of Fe_3O_4 nanoparticles shows a sharp linear increase versus field in the range of 0–100 Gs (Fig. S3d), indicating that the easy magnetization property of these particles when the field is less than 100 Gs. The above-mentioned results well demonstrated that the Fe_3O_4 magnetic nanoparticles mingled in the poly (VA-co-ED) monolith are superparamagnetic, and it can be magnetized and demagnetized easily under a small external magnetic field.

3.2. Optimization of MR/IT-SPME procedure

To achieve expected extraction performance for Co-DDTC, Cu-DDTC and Hg-DDTC, a series of key parameters including the intensity of magnetic field in adsorption and desorption steps, flow rates of sample and eluent, volumes of sample and eluent, sample pH value and co-existing ions were investigated thoroughly.

3.2.1. Intensity of magnetic field

According to the magnetic microfluidic principle [33], the magnetic field plays an important role in the enhancement of extraction for diamagnetic analytes. In this study, a magnetic field with the same direction as the sample flowing through the MCEN was applied in the adsorption step. To favor the release of analytes, a magnetic field with the reverse direction was used in the desorption step. The influences of the intensity of magnetic field in adsorption and desorption procedures on the extraction efficiency were investigated. As shown in Fig. 2a, the implementation of magnetic field in adsorption procedure can enhance the adsorption for analytes, thus improving the extraction efficiency of target complexes. The maximum extraction efficiencies could be obtained at 20 Gs. In desorption step, the effect of the intensity of magnetic field was studied by changing the intensity from 0 to 60 Gs (Fig. 2b). Results clearly indicate that the exertion of magnetic field in desorption procedure favors the release of retained analytes from MCEN. The most favorable intensity of magnetic field in desorption step was 40 Gs.

3.2.2. Flow rate and volume of sample

Typically, improving the flow rate of sample does not favor the

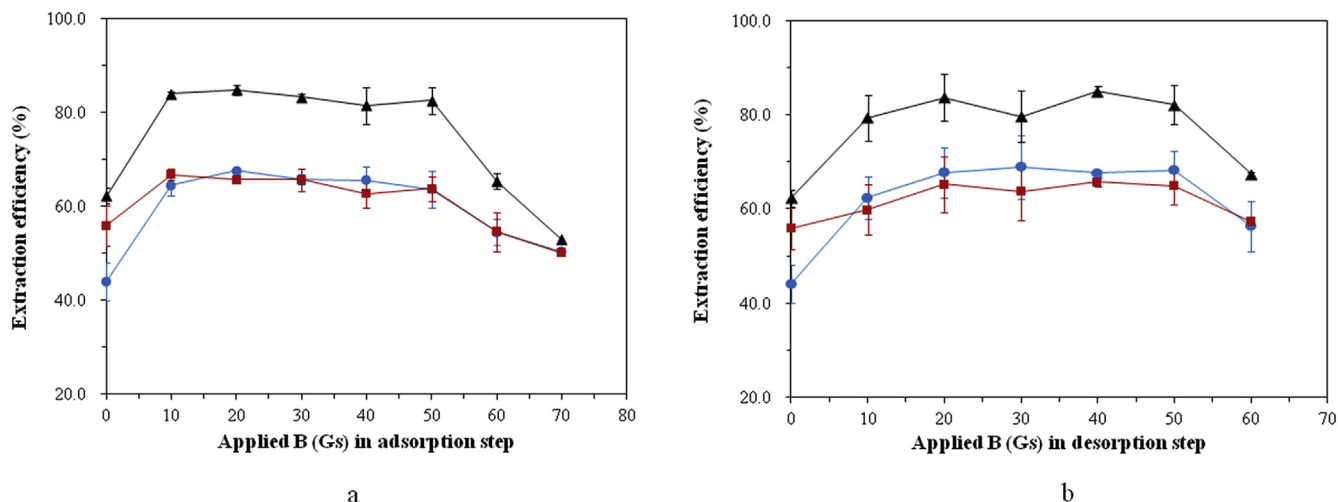


Fig. 2. Effects of the intensities of magnetic fields in adsorption (a) and desorption (b) steps on extraction efficiency. Conditions: (a) the intensity of magnetic field in desorption step, 40 Gs; the flow rate and volume of sample were 0.10 mL/min and 3.0 mL, respectively; the flow rate and volume of eluent (methanol) were 0.02 mL/min and 0.10 mL, respectively; the pH value of sample did not be adjusted. (b) the intensity of magnetic field in adsorption step, 20 Gs; the other conditions were the same as in Fig. 2a. The spiked concentrations of Co(II), Cu(II) and Hg(III) were 50.0, 50.0 and 100.0 $\mu\text{g/L}$, respectively, and the molar ratios of studied HMIs to DDTC were all 1:20; symbols: ● Co(II); ■ Cu(II); ▲ Hg(II).

extraction because there is not enough time for analytes to contact with adsorbent at high flow rate. In the present study, the influence of the flow rate of sample on extraction efficiency was evaluated by varying the flow rate from 0.08 to 0.20 mL/min with an interval of 0.02 mL/min. As indicated in Fig. 3a, there is no obvious change in extraction performance when flow rate of sample enhances from 0.08 to 0.14 mL/min. The result indicates that the implement of magnetic field in adsorption step favors the extraction of analytes at high flow rate. The sample volume affects the analytical time and sensitivity. As shown in Fig. 3b, the extraction efficiencies of Co-DDTC, Cu-DDTC and Hg-DDTC increase with the enhancement of sample volume from 2.0 mL to 4.0 mL, and decrease gradually when the volume is increased continuously. Based on the results, the flow rate and volume of sample were set at 0.14 mL/min and 4.0 mL, respectively, in the flowing experiments.

3.2.3. Flow rate and volume of eluent

In desorption procedure, the retained analytes can't be released

from the adsorbent completely at high flow rate of eluent. However, the favorable flow rate of eluent could be as high as 0.04 mL/min in the present study (Fig. S4a). The effect of the volume of eluent (methanol) on extraction efficiency was examined by increasing the volume from 0.04 to 0.12 mL (Fig. S4b). Results illustrate that 0.08 mL methanol can release the retained analytes from MCEN completely and the extraction efficiency reach the maximum. Therefore, the optimal flow rate of eluent was 0.04 mL/min and 0.08 mL methanol was selected as the most favorable desorption solvent.

3.2.4. Sample pH value

Sample pH value not only affects the existing forms of analytes and the surface properties of adsorbent, but also influences the complexation reaction, thus affecting the extraction efficiency. In this study, the influence of sample pH value was evaluated by varying the pH value from 4.0 to 9.0. As shown in Fig. S5, the extraction performance was poor at pH 4.0. The reason might be

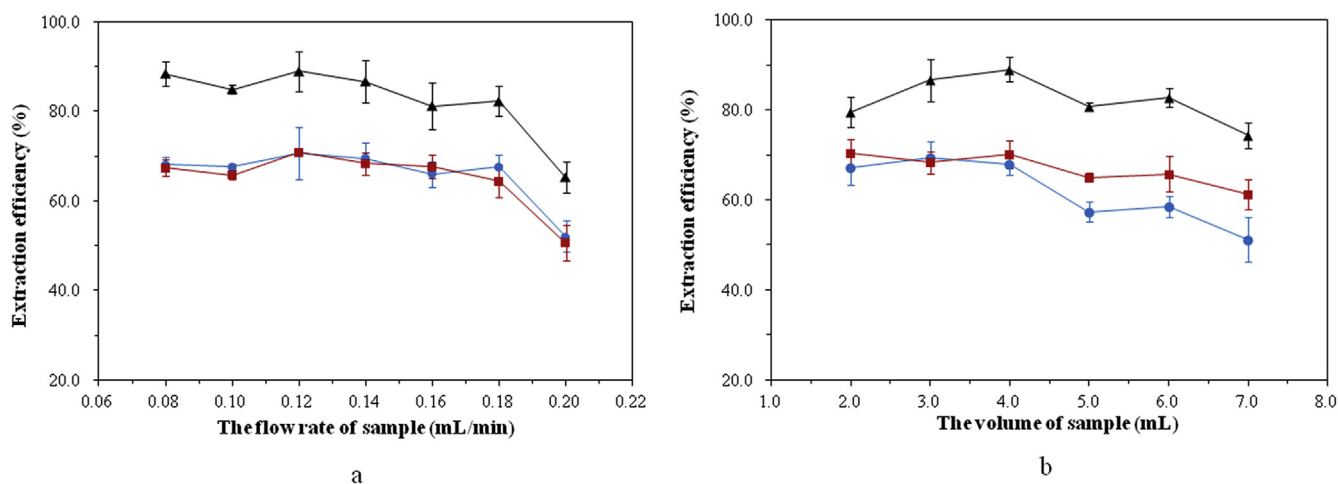


Fig. 3. Effects of the flow rate (a) and volume (b) of sample on extraction efficiency. Conditions: (a) the intensities of magnetic field in adsorption and desorption steps were 20 Gs and 40 Gs, respectively; the other conditions were the same as in Fig. 2; (b) the flow rate of sample, 0.14 mL/min; the other conditions were the same as in Fig. 4-a. The spiked concentrations of Co(II), Cu(II), Hg(II) and DDTC, and the symbols were the same as in Fig. 2.

that DDTC was unstable at low pH value, which made against the complexation reaction process. At the same time, protonated procedure occurred in the Co-DDTC, Cu-DDTC and Hg-DDTC, therefore, only π - π interaction contributed to the extraction. With the enhancement of pH value, more and more Co-DDTC, Cu-DDTC and Hg-DDTC were formed. In addition, deprotonated procedure occurred in the three complexes. Therefore, the hydrophobic, π - π and B-N interactions co-contributed to the extraction, resulting in the improvement of extraction performance. However, the extraction efficiencies declined quickly when the pH value was higher than 8.0 because that Co(II), Cu(II) and Hg(II) converted to precipitation of hydroxide at high pH value. Based on the discussion and experimental results, sample pH value was controlled at 7.0 in the following studies.

3.2.5. Co-existing ions

The influences of co-existing ions on the extraction performance of MR/IT-SPME were studied by adding different metal ions at different concentrations into a mixture containing 10.0 $\mu\text{g/L}$ Co(II), 10.0 $\mu\text{g/L}$ Cu(II) and 20.0 $\mu\text{g/L}$ Hg(II). The results indicated that, when the concentrations of K(I), Na(I), Ca(II) and Mg(II) were lower than 500 $\mu\text{g/L}$, and Zn(II), Pb(II), Cd(II), Fe(III) and Al(III) were lower than 10.0 $\mu\text{g/L}$, the recoveries of the analytes were higher than 80% and the effects of these co-existing ions could be negligible. The results indicated that the developed approach possessed acceptable selectivity due to the used DDTC could selectively coordinated with target HMLs under the current conditions.

According to the discussions above, the optimal conditions of MR/IT-SPME procedure in this study are as follows: the intensities of magnetic fields in adsorption and desorption steps were 20 Gs and 40 Gs, respectively; the flow rate and volume of sample were 0.14 mL/min and 4.0 mL, respectively; the sample pH value was adjusted to 7.0; the flow rate and volume of eluent (methanol) were 0.04 mL/min and 0.08 mL, respectively. In order to verify the magnetism-enhanced effect of magnetic field, the comparison experiments were carried out under the optimized conditions. Fig. 4 shows the HPLC chromatograms of Co-DDTC, Cu-DDTC and Hg-DDTC before extraction (Fig. 4a), treatment with IT-SPME (without magnetic field) (Fig. 4b) and MR/IT-SPME (Fig. 4c). The results well demonstrate that the proposed MR/IT-SPME method

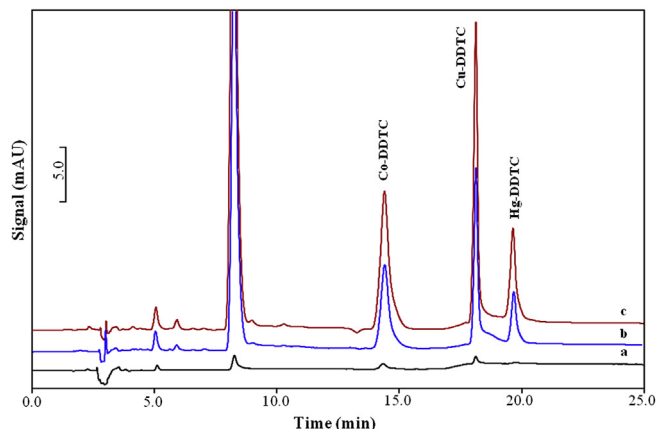


Fig. 4. HPLC chromatograms of Co-DDTC, Cu-DDTC and Hg-DDTC before treatment (a), after treatment with IT-SPME (b) and MR/IT-SPME (c). Conditions: (b) magnetic fields were not applied in adsorption and desorption steps; (c) the intensities of magnetic fields in adsorption and desorption steps were 20 Gs and 40 Gs, respectively. The flow rate and volume of sample were 0.14 mL/min and 4.0 mL, respectively; the sample pH value, 7.0; the flow rate and volume of eluent (methanol) were 0.04 mL/min and 0.08 mL, respectively; the spiked concentrations of Co(II), Cu(II) and Hg(II) were 10.0, 5.0 and 10.0 $\mu\text{g/L}$, respectively, and the molar ratios of targeted HMLs to DDTC were all 1:20.

can obviously improve the extraction performance for Co-DDTC, Cu-DDTC and Hg-DDTC, with the extraction efficiencies enhanced from 47–65% to 67–89%. The comparison means that higher sensitivity can be achieved when magnetic field is applied in the extraction procedure.

3.3. Validation of the online MR/IT-SPME-HPLC-DAD method

Table 1 exhibits the analytical characteristics of the optimized online MR/IT-SPME-HPLC-DAD method, including linear dynamic range, coefficient of determination (r^2), limit of detection (LOD), limit of quantification (LOQ) and precision. As shown, in water sample, the linear dynamic ranges for Co(II), Cu(II) and Hg(II) are 0.050–150.0 $\mu\text{g/L}$, 0.025–150.0 $\mu\text{g/L}$ and 0.50–150.0 $\mu\text{g/L}$, respectively. Each ion displayed good linearity, the r^2 values vary from 0.9967 to 0.9988. In fish sample, the linear ranges for Co(II) and Hg(II) are in the range of 25.0–15000 $\mu\text{g/kg}$, and 5.0–15000 $\mu\text{g/kg}$ for Cu(II). The r^2 values are all higher than 0.9940. The LOD and LOQ values were calculated at a signal-to-noise ratio of $S/N = 3$ and $S/N = 10$, respectively. As indicated in Table 1, for water sample, the LOD and LOQ values are in the range of 0.0043–0.035 $\mu\text{g/L}$ and 0.014–0.12 $\mu\text{g/L}$, respectively. For seafood sample, the corresponding values are 0.69–4.9 $\mu\text{g/kg}$ and 2.2–16 $\mu\text{g/kg}$, respectively. The LODs for water and seafood samples are far below the related MRLs regulated by the European Union (EU) [34] and Chinese government [35]. In addition, the precision of the proposed method was evaluated by studying the intra-day and inter-day assay variability with low and high fortified concentrations. The results listed in Table 1 indicate that relative standard deviation (RSD) values are in the ranges of 2.6–8.7% and 1.4–9.1% for water and seafood samples, respectively. It is worth being mentioned that the MCEN possessed satisfactory life span, it could be reused to enrich studied compounds more than 50 times without loss of extraction performance during continuous application. The above-mentioned results well evidence that the developed online MR/IT-SPME-HPLC-DAD method exhibits satisfactory sensitivity and precision, it can be applied to analyze trace levels of Co(II), Cu(II) and Hg(II) in real samples.

3.4. Analysis of real samples

To test and verify the applicability of proposed online MR/IT-SPME-HPLC-DAD method, it was applied to analyze the target ions in environmental waters (tap, lake and well waters) and seafood samples (fish and shrimp). As listed in Table 2, Co(II) and Hg(II) concentrations in the three water samples were below the established LOD values. Trace levels of Cu(II) were detected in the three waters. For seafood samples, 40.3 $\mu\text{g/kg}$ Cu(II) was found in fish sample 1. In fish sample 2, the concentrations of the detected Co(II) and Cu(II) were 29.0 $\mu\text{g/kg}$ and 20.2 $\mu\text{g/kg}$, respectively. The Cu(II) level in shrimp sample was 347.8 $\mu\text{g/kg}$. In the all seafood samples, Hg(II) did not be detected. Fig. S6 displays the typical chromatograms obtained from blank river water and seafood samples.

To evaluate the matrix-effect and accuracy of the proposed method, fortified recovery with three different spiked concentrations were studied. As shown in Table 2, the recoveries are in the range of 81.1–117% and 72.6–116% for water and seafood samples, respectively. Furthermore, the RSD values for precision are below 10% for all analytes in all samples. To further assess the accuracy of the developed MR/IT-SPME-HPLC-DAD method, confirmatory experiments with reference methods by analyzing three waters and four seafood samples were carried out. It can be seen from the data listed in Table S1 that the concentrations detected with the proposed method are well in agreement with those obtained with LLE-AAS [36] (for water samples) and GB5009.268–2016 (for seafood

Table 1
Analytical features of the developed online MR/IT-SPME-HPLC-DAD method for the determination of Co(II), Cu(II) and Hg(II).

Samples	Ions	Linear range ^a (μg/L or μg/kg)	r ²	LOD ^b (μg/L or μg/kg)	LOQ ^c (μg/L or μg/kg)	Intra-day assay variability (RSD, %, n = 4) spiked concentration		Inter-day assay variability (RSD, %, n = 4) spiked concentration	
						Low ^d	High ^d	Low ^d	High ^d
Water	Co(II)	0.050–150.0	0.9988	0.013	0.042	3.8	4.9	5.6	5.2
	Cu(II)	0.025–150.0	0.9980	0.0043	0.014	5.9	5.1	8.7	3.8
	Hg(II)	0.500–150.0	0.9967	0.035	0.12	5.4	2.6	2.6	3.1
Fish	Co(II)	25.0–15000	0.9962	4.9	16	7.9	7.8	6.2	7.8
	Cu(II)	5.0–15000	0.9940	0.69	2.2	8.9	6.4	7.5	3.5
	Hg(II)	25.0–15000	0.9976	4.2	14	2.8	7.6	9.1	1.4

^a For water sample: spiked level included 0.025, 0.05, 0.10, 0.25, 0.5, 1.0, 2.0, 5.0, 10.0, 50.0, 100.0, and 150.0 μg/L, respectively. For fish sample: spiked level included 5.0, 10.0, 25.0, 50.0, 100.0, 200.0, 500.0, 1000, 5000, 10000 and 15000 μg/kg, respectively.

^b S/N = 3.

^c S/N = 10.

^d For water sample: low spiked concentration at 0.5 μg/L level and high spiked concentration at 50.0 μg/L level. For fish sample: low spiked concentration at 50.0 μg/kg level and high spiked concentration at 5000 μg/kg level.

Table 2
Results of determination and spiked recoveries of Co(II), Cu(II) and Hg(II) in water and seafood samples.

Samples	Spiked (μg/L or μg/kg)	Detected (μg/L or μg/kg)/recovery (%RSD, n = 3)					
		Co(II)		Cu(II)		Hg(II)	
Tap water	0.0	ND ^a		1.39		ND	
	0.5	0.47	94.7 (6.7)	1.91	104 (6.4)	0.53	105 (7.5)
	5.0	4.63	92.7 (1.9)	7.26	117 (2.1)	4.33	86.7 (3.7)
	50.0	45.5	91.1 (9.0)	56.5	110 (5.8)	49.4	98.7 (7.5)
Well water	0.0	ND		0.55		ND	
	0.5	0.44	88.1 (7.6)	0.97	83.8 (1.4)	0.55	109 (7.6)
	5.0	4.39	87.7 (5.2)	4.98	88.5 (3.2)	4.33	86.6 (9.5)
	50.0	46.1	92.1 (1.0)	50.7	100 (2.2)	47.3	94.5 (1.5)
River water	0.0	ND		0.45		ND	
	0.5	0.43	86.5 (8.4)	0.87	82.7 (3.1)	0.54	107 (8.9)
	5.0	4.11	82.1 (2.9)	4.70	84.8 (5.7)	4.36	87.2 (4.8)
	50.0	40.5	81.1 (0.5)	44.5	88.1 (2.6)	43.5	87.0 (1.7)
Fish 1	0.0	ND		40.3		ND	
	50.0	46.7	93.3 (6.2)	85.8	91.0 (2.3)	57.9	116 (3.3)
	500.0	493.2	98.6 (7.3)	504.8	92.9 (2.3)	519.0	104 (5.4)
	5000	5383	108 (0.6)	4613	91.4 (3.4)	4468	89.4 (2.0)
Fish 2	0.0	29.0		20.2		ND	
	50.0	73.0	88.0 (8.3)	69.6	98.7 (5.7)	53.3	107 (4.9)
	500.0	542.7	103 (4.9)	456.9	87.3 (4.8)	470.0	94.0 (2.8)
	5000	4572	90.9 (1.6)	4106	81.7 (8.0)	4268	85.4 (5.8)
Shrimp	0.0	ND		347.8		ND	
	100.0	76.5	76.5 (3.6)	460.2	112 (6.7)	85.3	85.3 (5.1)
	1000	898.8	89.9 (4.4)	1272.3	92.4 (9.1)	872.9	87.3 (9.4)
	5000	4146	82.9 (3.5)	3976	72.6 (2.1)	3728	74.6 (2.9)

^a Not detected.

samples) [37]. The above results well evidence that the MR/IT-SPME-HPLC-DAD method possesses satisfactory accuracy and precision.

3.5. Comparison with previous methods

To further demonstrate the merits of the developed method, the LOD values and spiked recoveries obtained in this method were compared with that achieved in reported methods. As indicated in Table S2, for the determination of Co(II), Cu(II) and Hg(II) in water samples, the LODs achieved in the proposed method are lower than that obtained in LLE-AES [38], LLE-AAS [36], DLLME-HPLC-UV [39], DLLME-ICP-AES [40], MSPE-AES [41,42] and CPE-AAS [21]. Typically, better sensitivity can be achieved in ICP-MS [43]. However, for the determination of Cu(II), the present method displays better sensitivity than MSPE-ICP-MS [44]. For the analysis of studied HMIs in seafood samples, the developed approach exhibits the lower LODs than EME-UV [45], CPE-AAS [21], DLLME-AAS [46] and MSPE-

AAS [47]. The comparison also indicates that the spiked recoveries achieved in the suggested approach are comparable with that obtained in the existing methods [21,36,38,40–45,47]. Furthermore, the extraction and determination procedures in previous methods are offline. However, the proposed MR/IT-SPME is online combined with HPLC-DAD, which not only saves labor and time, but also increases the analytical accuracy and precision. Therefore, the suggested approach is more simple and convenient, and suitable for the routine trace analysis of HMIs.

4. Conclusions

In summary, we developed a novel analytical method for the online determination of Co(II), Cu(II) and Hg(II). The targeted ions were firstly coordinated with DDTC to form three diamagnetic metallic coordination compounds Co-DDTC, Cu-DDTC and Hg-DDTC, and then enriched by a monolith-based microextraction column which embedded Fe₃O₄ nanoparticles. According to the

magnetic microfluidic principle, implement of magnetic field during adsorption and desorption steps could obviously improve the extraction efficiency of three complexes. Under the most favorable conditions, the extraction efficiencies were 67–89%, which were obviously higher than that obtained in the conventional IT-SPME mode (47–65%). The proposed online MR/IT-SPME-HPLC-DAD system was successfully applied to detect studied ions in environmental water and seafood samples, and displayed some advantages such as automation, cost-effectiveness, satisfactory sensitivity, good precision and environmental friendliness. Therefore, we believe that the proposed method is a competitive alternative in the analysis of trace levels of HMIs in complex samples.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2019.09.028>.

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