Talanta 116 (2013) 361–367

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

# Magnetic solid-phase extraction combined with graphite furnace atomic absorption spectrometry for speciation of Cr(III) and Cr(VI) in environmental waters

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ARTICLE INFO

*Article history:*
Received 20 February 2013
Received in revised form
3 May 2013
Accepted 6 May 2013
Available online 24 May 2013

*Keywords:*
Magnetic nanoparticles
Zincon
Solid phase extraction (SPE)
Chromium
Speciation
Graphite furnace atomic absorption spectrometry (GFAAS)

ABSTRACT

A new approach of magnetic solid phase extraction (MSPE) coupled with graphite furnace atomic absorption spectrometry (GFAAS) has been developed for the speciation of Cr(III) and Cr(VI) using zincon-immobilized silica-coated magnetic $Fe_3O_4$ nanoparticles (Zincon–Si–MNPs) as the MSPE absorbent. Cr(III) was quantitatively reserved on the absorbent at pH 9.1 while total Cr was reserved at pH 6.5. The absorbed Cr species were eluted by using 2 mol/L HCl and detected by GFAAS. The concentration of Cr(VI) could be calculated by subtracting Cr(III) from total Cr. All the parameters affecting the separation and extraction efficiency of Cr species such as pH, extraction time, concentration and volume of eluent, sample volume and influence of co-existing ions were systematically examined and the optimized conditions were established accordingly. The detection limit (LOD) of the method was 0.016 and 0.011 ng $mL^{-1}$ for Cr(III) and Cr(VI), respectively, with the enrichment factor of 100 and 150. The precisions of this method (Relative standard deviation, RSD, $n=7$) for Cr(III) and Cr(VI) at 0.1 ng $mL^{-1}$ were 6.0% and 6.2%, respectively. In order to validate the proposed method, a certified reference material of environmental water was analyzed, and the result of Cr speciation was in good agreement with the certified value. This MSPE–GFAAS method has been successfully applied for the speciation of Cr(III) and Cr(VI) in lake and tap waters with the recoveries of 88–109% for the spiked samples. Moreover, the MSPE separation mechanism of Cr(III) and Cr(VI) based on their adsorption–desorption on Zincon–Si–MNPs has been explained through various spectroscopic characterization.

## 1. Introduction

Chromium and its compounds are widely used in electroplating, leather tanning, metal cleaning, dying, photography industries and textile industries [1], so the chromium species are very easy to release into the water bodies. The most common and stable forms of chromium are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)). Cr(III) is considered as an essential micronutrient for human, plant and animal metabolism, and relatively non-toxic, while Cr(VI) is toxic and bioavailable in the environment and carcinogenic to living organism [2]. Given the above considerations, specific attention has been devoted to establish fast, sensitive and reliable analytical methods for the speciation of Cr(III) and Cr(VI) in environmental waters, where the typical concentration of total Cr is in the range of 0.1–0.5 μg $L^{-1}$ [3].

In usual conditions, there is no selectivity to different valent state of element by conventional analytical instrumentation such as atomic adsorption spectrometry (AAS), inductively coupled plasma–atomic emission spectrometry (ICP–AES) and inductively coupled plasma–mass spectrometry (ICP–MS). Thus, without using direct chromatographic method, the most effectual strategy for speciation of Cr(III) and Cr(VI) is to combine selective separation and/or preconcentration procedure with sensitive detection techniques. In this mode of speciation, one of the chromium species (Cr(III) or Cr(VI)) is determined by means of separation/preconcentration coupling with different detection methods, and total chromium is determined after reduction of Cr(VI) or oxidation of Cr(III) according to the bases of above procedure. For this purpose, the separation and preconcentration methods reported in the literature are usually based on coprecipitation [4–6], cloud point

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*Abbreviations:* Zincon–Si–MNPs, zincon-immobilized silica-coated magnetic $Fe_3O_4$ nanoparticles; SPE, solid-phase extraction; GFAAS, graphite furnace atomic absorption spectrometry; ICP–OES, inductively coupled plasma optical emission spectrometry; ICP–MS, inductively coupled plasma–mass spectrometry; FAAS, flame atomic absorption spectrometry; MNPs, magnetic $Fe_3O_4$ nanoparticles; Si–MNPs, silica-coated magnetic $Fe_3O_4$ nanoparticles; LOD, limit of detection; RSD, relative standard deviation.

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http://dx.doi.org/10.1016/j.talanta.2013.05.008

extraction (CPE) [7–9] and solid phase extraction (SPE) [3,10,11]. Among these methods, SPE has become a very powerful and effective sample pretreatment method due to the advantages such as high recovery, short analysis time, high enrichment factor and low consumption of organic solvents. In SPE procedure, the key is focused on seeking a proper absorbent in order to obtain full recovery, high enrichment factor, good selectivity, large capacity and fast extraction. To date, a variety of absorbents has been used for the speciation of Cr(III) and Cr(VI), for instance, chelating resin [3,12–14], olive pomace [11], multiwalled carbon nanotubes [15], polystyrene [16], nanometer titanium dioxide [17], silica gel [18] and aluminum oxide [19]. However, these absorbents usually need relatively long extraction time especially when dealing with large sample volume, so the special interest and efforts have been concentrated in the design of new type of efficient absorbents by numerous analysts.

Magnetic nanoparticles (MNPs) are the kind of aborbents and the most attractive property of MNPs is that they have a superparamagnetic behavior under certain particle size, which implies that it could be easily magnetized and gathered together with an external magnetic field and redispersed immediately once the magnet field is removed [20]. Another exciting characteristic of MNPs is the bio-compatibility because most of MNPs are iron oxide like magnetite ($Fe_3O_4$), maghemite ($Fe_2O_3$) and cobalt ferrite ($CoFe_2O_4$) which can be easily dissolved in blood [21]. The third important feature of MNPs is the large surface area that can be properly modified by different reagents to attach biological agents. So MNPs are initially and extensively used in biomedical [22] and biotechnological applications [23]. Just because of the above three charming advantages, MNPs have gained more and more attention by many analysts in recent years and have been applied in environmental analysis [24] through magnetic SPE process. When MNPs are used as absorbent of magnetic SPE, they are often surface modified by different specific organic reagents because naked MNPs are easy to aggregate, and not selective and not suitable for the samples with complicated matrix [25].

In the past five years, several modifying reagents such as γ-mercaptopropyltrimethoxysilane [26], 2-amino-5-mercapto-1,3,4-thiadiazole [27], bismuthiol-II [28] and decanoic acid [29] have been reported for the separation and concentration of metal ions. Until quite recently, however, only a few works about application of MSPE have been reported for speciation of element. Huang et al. [30] developed a new protocol for the speciation of inorganic arsenic in environmental water. In their study, As(V) can be selectively absorbed on amino-modified silicacoated MNPs and As(III) was not be retained, so total inorganic As could be determined after the oxidation of As(III) to As(V). In our foregoing study [31], the new sorbent named zincon-immobilized silica-coated magnetic $Fe_3O_4$ nanoparticles (Zincon–Si–MNPs) has been proposed for the first time and employed for the extraction and determination of trace lead in natural and drinking waters. In the following research, we find that Zincon–Si–MNPs can quantitaqtively reserve Cr(III) and Cr(VI) respectively in different pH range. Based on aforesaid founding, the work reported here aims at developing a new proposal for speciation of Cr(III) and Cr(VI) by using MSPE coupled with graphite furnace (GF) AAS.

## 2. Materials and methods

### 2.1. Apparatus

A Hitachi Z-2000 atomic absorption spectrometer (Hitachi, Japan), coupled with a heated graphite tube atomizer was used to determine chromium. A Cr hollow cathode lamp (Hitachi, Japan) operated at 6.5 mA was employed as the radiation source. The wavelength used for monitoring Cr was 357.9 nm with a spectral band width of 1.3 nm. A KQ3200DE ultrasonic bath (Suzhou, China) was applied to disperse the nanoparticles in solution. An Nd–Fe–B magnet (8.0 mm × 6.0 mm × 1.6 mm) was used for magnetic separation (Nanjing, China). The adsorption mechanism was characterized by TENSOR27 Fourier transform infrared spectrometer (FI-IR) (Bruker, Germany) and PHI 5000 VersaProbe X-ray photoelectron spectroscopy (XPS) (ULVAC-PHI, Japan).

### 2.2. Standard solution and reagents

The stock standard solution for Cr(III) (1000 mg $L^{-1}$) and Cr(VI) (1000 mg $L^{-1}$) was provided by China National Measuring Science Research Institute (Beijing, China). All standard solutions were prepared by appropriate dilution of the stock solutions daily and all reagents were at least analytical grade. Highly pure deionized water (18.2 MΩ cm) obtained from a Labconco system (Labconco, MO, USA) was utilized throughout the whole work. Plastic, glass containers and all other immersed laboratory materials that could come into contact with samples or standards were all dipped in 20% (v/v) nitric acid for 24 h, and then rinsed with water prior to use. Zincon was bought from First Reagent Factory (Shanghai, China). Tetraethoxysilane (TEOS) were purchased from Aladdin's reagent network (Shanghai, China). Certified Reference Material of Environment Water (GBW08607) was supplied by China National Measuring Science Research Institute.

### 2.3. Procedure for the speciation of Cr(III) and total Cr by magnetic solid phase extraction

The preparation of Zincon–Si–MNPs was the same as our previous work [31]. Briefly, magnetic $Fe_3O_4$ nanoparticles (MNPs) prepared through co-precipitation of $FeCl_3$ and $FeCl_2$ were wrapped up in a layer of silica by condensation with hydrolytic silylating reagent TEOS, and finally coated with zincon. The Zincon–Si–MNPs were characterized by FT-IR, transmission electron microscope (HRTEM) and X-ray diffraction (XRD) [31]. For a batch of the well-characterized absorbent, there is no obvious reduction in recovery after the whole MSPE speciation procedure in standard solutions and real water samples in triplicate. The speciation scheme of Cr(III) and total Cr is illustrated in Fig. 1.

For Cr(III): 100 mL of aqueous sample solution were put into a glass beaker and then adjusted to pH 9.1 with 1 mol $L^{-1}$ HCl or 27% (w/w) of aqueous solution of ammonia. 20 mg of Zincon–Si–MNPs was subsequently thrown into the solution and the mixture was ultrasonicated for 3 min to facilitate adsorption of the metal ions on the nanoparticles. Then the absorbent were gathered together and collected at the bottom of the beaker by an external magnetic field and the supernatant was discarded. Then, 1 mL 2 mol $L^{-1}$ HCl was added into the beaker as eluent and the new mixture was ultrasonicated for 3 min again. Finally, the magnetic absorbent was removed through an external magnetic field again and the supernatant was collected for Cr determination by GFAAS.

For total Cr: The MSPE procedure for total Cr was nearly the same as that of Cr(III) except the pH of sample solution was adjusted to 6.5 prior to extraction.

Highly pure deionized water was selected as the blank solution and carried out magnetic SPE procedure described above. The determined values for Cr(III) and total Cr were obtained after substracting the blank values.

### 2.4. Sample preparation

Xuanwu Lake water was sampled from Xuanwu Lake in Nanjing, China and tap water was collected from the local supply system in Nanjing, China. Before use, the lake water was filtered through

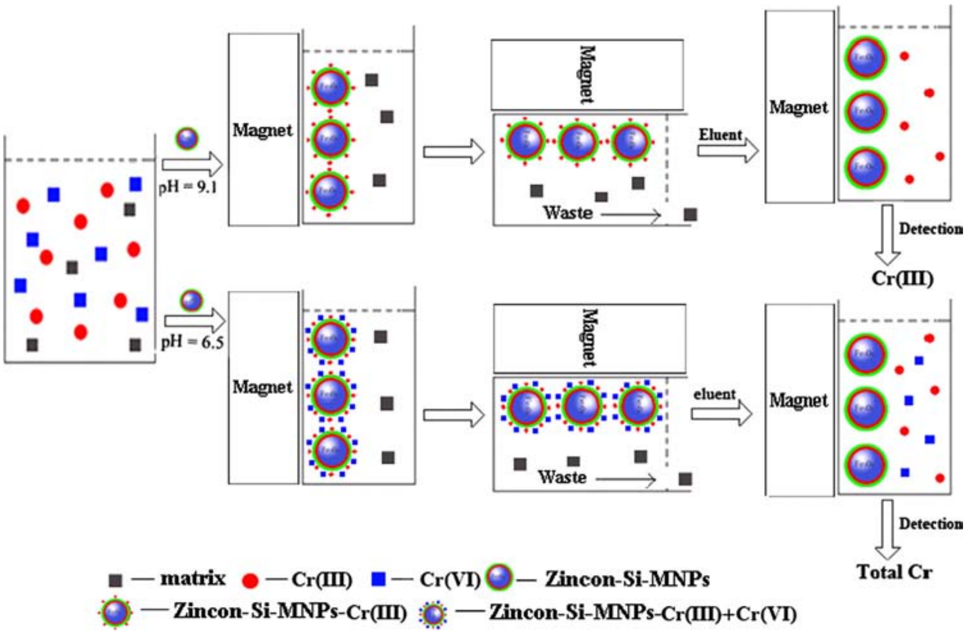

**Fig. 1.** The speciation scheme of Cr(III) and total Cr.

a 0.45 μm membrane filter (Tianjin, China). The pH value of the two water samples were both adjusted to 6.5 and 9.1, respectively. The pH of Certified Reference Material of Environment Water (GBW08607) was adjusted to 6.5 and 9.1 respectively after 1000 fold dilution.

## 3. Results and discussion

Several parameters were examined systematically to establish optimal MSPE conditions for the speciation of Cr(III) and total Cr, including pH, elution and ultrasonic time, sample volume, and co-existing ions, etc.

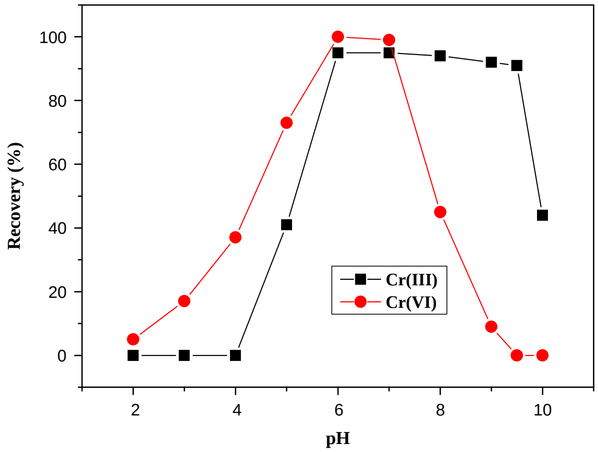

**Fig. 2.** The effect of pH on the recovery of Cr(III) and Cr(VI) on Zincon-Si-MNPs.

### 3.1. Effect of pH

pH of sample solution plays an important role on adsorption efficiency, and therefore is proved to be a primary parameter for SPE or MSPE. Moreover, a proper pH can bring down the interference of the matrix and increase the selectivity of the method. The adsorption behavior of Cr(III) and Cr(VI) on Zincon–Si–MNPs was investigated based on the experimental procedure and the results are shown in Fig. 2. As can be seen that the recovery of Cr (III) increased with the increase of pH from 2.0 to 6.0, and then remained constant quantitatively, and finally decreased sharply after $pH > 9.5$. The trend of the effect of pH on the recovery of Cr (VI) was similar with Cr(III), but the platform pH ranged from 6.0 to 7.0. According to the above results, we found that both Cr(III) and Cr(VI) are quantitatively reserved on Zincon–Si–MNPs in the pH range of 6.0–7.0, while only Cr(III) is retained on the absorbent in the pH range of 9.0–9.5. So, speciation of Cr(III) and Cr(VI) can be attained, and notably, no reduction and oxidation process is needed prior to MSPE operation. For further study, pH 6.5 was chosen for preconcentration of total Cr and pH 9.1 was selected for speciation of Cr(III).

The different adsorption behavior of Cr(III) and Cr(VI) on Zincon–Si–MNPs is due to the existence form of Cr(III) and Cr(VI) in different pH conditions and surface nature of the absorbent. In view of Cr(III), on one hand, it tends to be hydrolyzed in aqueous solution at $pH > 4$ and forms several positively charged species including $Cr^{3+}$ and $Cr(OH)^{2+}$ [32], and then can be chelated with N atom of zincon, which leaded to increasing recovery from pH 4.0 to 6.0 and moreover quantitative recovery when pH was bwteen 6.0 and 9.5. After $pH > 9.5$, however, the cations of Cr(III) is prone to form precipitate, resulting in rapid decrease in the recovery. Another reason for little recovery of Cr(III) below pH 4.0 is the strong acidc effect on chelation of zincon to Cr(III). With respect to Cr(VI), it exists mainly in the form of $HCrO_4^-$ in the pH range from 2 to 7, associated with small concentration of $H_2CrO_4$ and $CrO_4^{2-}$, as well as a portion of $Cr_2O_7^{2-}$ formed by condensation of two $HCrO_4^-$ ions at weak acidic solution. While $CrO_4^{2-}$ is the predominant species of Cr(VI) when $pH > 7$, associated with small and tiny concentration of $HCrO_4^-$ and $H_2CrO_4$, respectively [33]. In acidic medium, the electrostatic interaction may occur between the anions of Cr(VI) and protonated N-containg groups on the surface of Zincon–Si–MNPs, and therefore, Cr(VI) anions were reserved on the absorbent. Moreover, the recovery of Cr(VI) increased as the pH increased from 2.0 to 6.0 and approched 100% when pH was 6.0–7.0. After $pH > 7.0$, however, the anions of Cr(VI) cannot be absorbed because of the electrostatic repulsion of dissociated phenolic hydroxyl group and the negatively charged surface of Zincon–Si–MNPs, which caused significant decrease in recovery of Cr(VI).

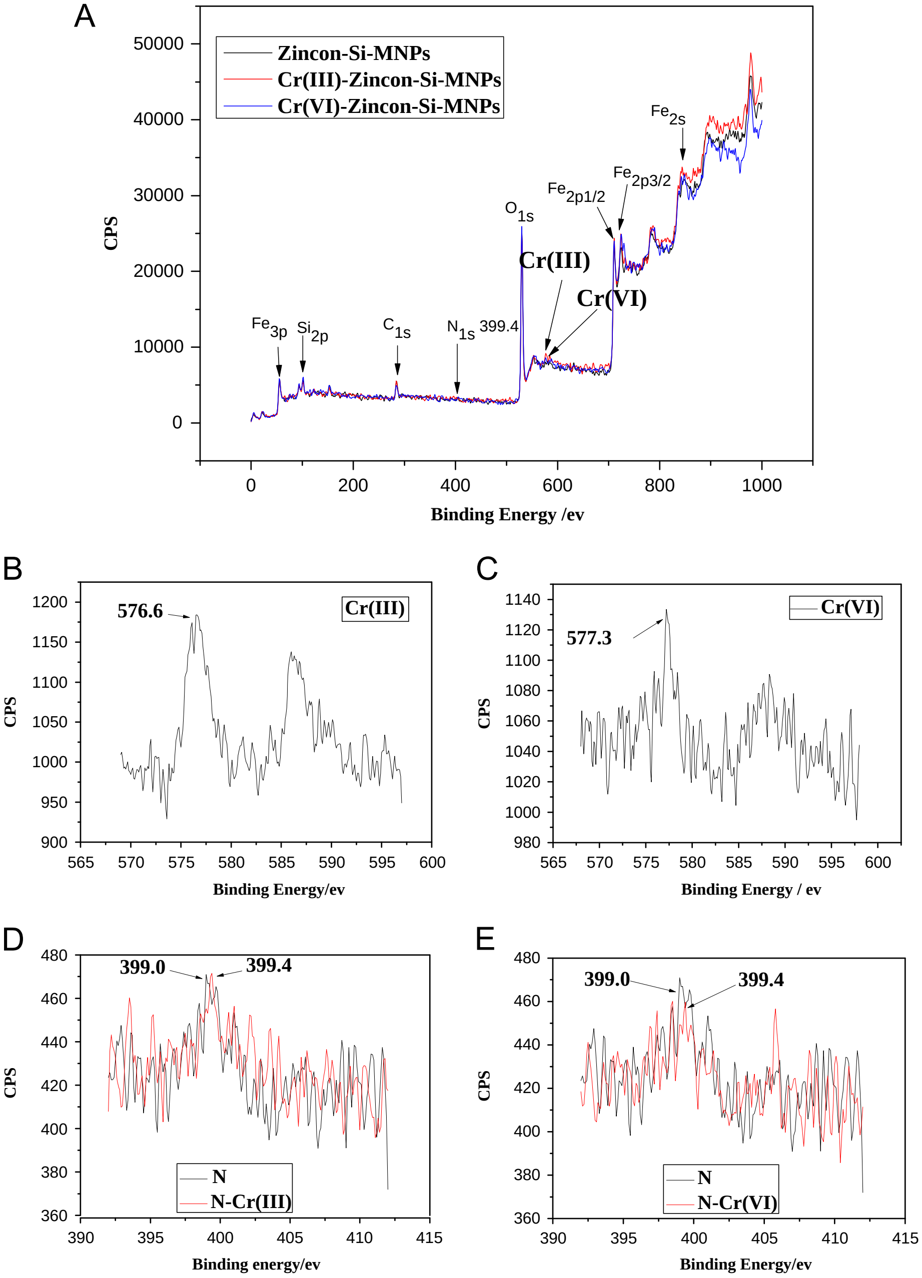

**Fig. 3.** XPS spectra of Zincon–Si–MNPs before and after extraction (A), Cr(III)- Zincon–Si–MNPs, (B) Cr(VI)-Zincon–Si–MNPs, (C) N1s and N1s-Cr(III) (D) N1s and (E) N1s-Cr (VI).

XPS can not only identify the existence of an element, but also distinguish the valence of the element. In order to validate the elucidation mentioned above about adsorption mechanism of Cr (III) and Cr(VI) on Zincon–Si–MNPs, the characterization for attraction of the absorbent to Cr(III) and Cr(VI) was performed by XPS first. The pure Zincon–Si–MNPs, Zincon–Si–MNPs absorbing Cr(III) (Cr(III)–Zincon–Si–MNPs) and Zincon–Si–MNPs absorbing Cr (VI) (Cr(VI)–Zincon–Si–MNPs) were all collected for the XPS measurement and the results are shown in Fig. 3. It has been noticed that Fe, O, C and N were the main existing elements in all three XPS spectra, however, the element Cr was only existed in the latter two spectra and the percentage of these elements are listed in Table 1. According to the Handbook of X-Ray Photoelectron Spectroscopy edited by Perkin-Elmer Corp. [34], the significant band with binding energy of 576.6 eV founded in Fig. 3 (B) corresponds to Cr(III). It is very interesting that the binding energy of Cr in Cr(VI)-Zincon-Si-MNPs was 577.3 eV as shown in Fig. 3(C), which also corresponds to Cr(III). This phenomenon can be explained as follows. The standard electrode potentials for reduction of $HCrO_4^-$ and $Cr_2O_7^{2-}$ to $Cr^{3+}$ in acidic medium are 1.35 V and 1.33 V, respectively. These powerful oxidizing Cr(VI) species adsorbed on the surface of Zincon–Si–MNPs are very easy to be reduced by phenolic group of zincon [35]. The formed Cr(III) was subsequently chelated with zincon like the native Cr(III) in

**Table 1**
The percentage of main elements in Zincon–Si–MNPs, Cr(III)- and Cr(VI)–Zincon–Si–MNPs by XPS.

| Sample | $C_{1s}$ (%) | $N_{1s}$ (%) | $O_{1s}$ (%) | $Fe_{2p}$ (%) | $Cr_{2p}$ (%) |
|---|---|---|---|---|---|
| Zincon–Si–MNPs | 18.87 | 1.52 | 59.17 | 20.44 | / |
| Cr(III)–Zincon–Si–MNPs | 22.14 | 1.40 | 56.12 | 18.47 | 1.87 |
| Cr(VI)–Zincon–Si–MNPs | 15.72 | 0.95 | 60.00 | 22.40 | 0.93 |

original solution. In Fig. 3(D), the peak appeared at 399.0 eV was attributed to N atoms in zincon and the bind energy was shifted to 399.4 eV after absorbing Cr(III). Similar shift was observed for Cr (VI)–Zincon–Si–MNPs in Fig. 3(E), and the possible reason for this was due to the formation of Cr(III)–N that could decrease the electronic density around N atoms [36]. Both the results revealed that Cr(III) and Cr(VI) have been bound to Zincon–Si–MNPs in spite of different interaction.

To confirm the main function group before and after adsorption in the absorbent, FT-IR spectroscopy was employed in this study. Fig. 4 is the IR spectra of Zincon–Si–MNPs, Cr(III)–Zincon–Si–MNPs and Cr(VI)–Zincon–Si–MNPs. It appears that the peaks at 560–590 cm$^{-1}$ and 450 cm$^{-1}$ are related to Fe–O group, the peaks around 1086 cm$^{-1}$ and 1500 cm$^{-1}$ are assigned to C–O stretching vibration and skeletal vibration of benzene ring, respectively, which were all found in three IR spectra mentioned above. The remarkable difference in the three IR spectra was the peak about 1400 cm$^{-1}$, corresponding to N–H in-plane bending vibration, was only appeared in the naked Zincon–Si–MNPs, which was accorded very well with the result of XPS and further demonstrated that Cr (VI) is reduced to Cr(III) and then chelated with N atoms in Zincon–Si–MNPs. These results suggested that the combination of electrostatic interaction and chelation is one kind of SPE mechanism.

### 3.2. *Effect of eluent*

The choice of the suitable eluent is important for the analytical performance of the MSPE procedure. In order to quantitatively elute the absorbed Cr species from Zincon-Si-MNPs, HCl was selected as eluent since the recovery of Cr(III) and Cr(VI) were both less than 5% when pH≤2. So, the effects of concentration of HCl on the recovery of Cr(III) and total Cr were explored. The concentration of HCl was examined in the range of 0.1–2 mol L$^{-1}$ and the results showed that both the recoveries of Cr(III) and total Cr increased with the increase of HCl concentration during the investigated concentration range and can reach 90% when HCl concentration was 2 mol L$^{-1}$. Meanwhile, the results about the influence of the volume of 2 mol L$^{-1}$ HCl on the recovery of Cr(III) and total Cr indicated that they can be quantitatively desorbed from Zincon–Si–MNPs in the volume range of 1–5 mL. For the purpose of achieving high enrichment factor, a small volume of 1 mL 2 mol L$^{-1}$ HCl was used to elute Cr(III) and total Cr in this work.

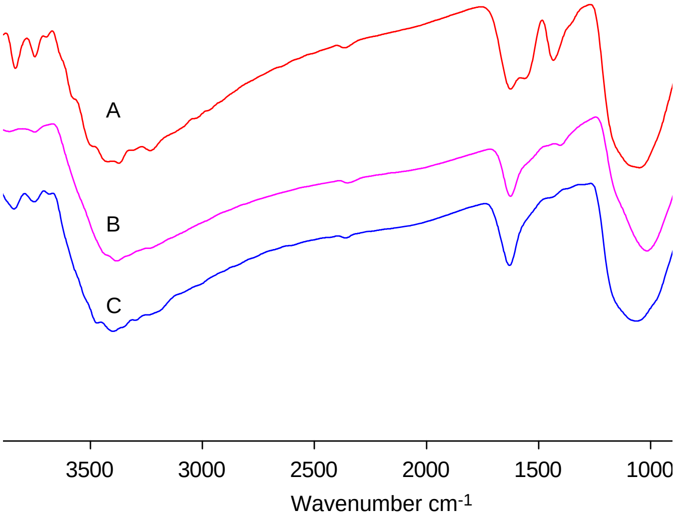

**Fig. 4.** (A) FT-IR spectra of Zincon–Si–MNPs, (B) Cr(III) and (C) Cr(VI)–Zincon–Si–MNPs.

### 3.3. *Effect of ultrasonic time*

Ultrasonic time is another important parameter in MSPE and shorter time is needed in MSPE than ordinary SPE method especially when dealing with large sample volume. Thus, the effects of ultrasonic time on the adsorption and desorption were evaluated respectively and the ultrasonic time was varied from 1 min to 10 min for both adsorption and desorption. The results showed that satisfactory recoveries for Cr(III) and total Cr can be obtained during adsorption and desorption procedure after 2 min, which indicated that this MSPE is a very fast extraction process. Finally, 3 min was selected as adsorption and desorption time.

### 3.4. *Effect of sample volume*

In order to obtain reliable and reproducible analytical results and a high concentration factor, it is very important to get desirable recoveries for Cr(III) and total Cr in as large sample volume as possible. So it is necessary to receive the maximum sample volume in MSPE. The effects of sample volume ranging from 10 mL to 200 mL on the recovery of Cr(III) and total Cr are investigated and the results showed that quantitative recoveries ( > 90%) can be obtained when sample volumes were less than 100 mL and 150 mL, respectively, for Cr(III) and total Cr. Thus, a water sample volume of 100 mL was selected in this method.

### 3.5. *Influence of co-existing ions*

To examine the selectivity of the proposed MSPE method for the speciation of Cr(III) and Cr(VI), the competitive adsorption of alkali, alkaline earth and heavy metals, which are common elements in environmental waters, were investigated as well and the results are summarized in Table 2. The results demonstrated that these co-existing ions have no obvious interfere with the determination of Cr(III) and total Cr and the developed method is suitable for the speciation of Cr(III) and Cr(VI) in natural and tap waters.

### 3.6. *Analytical performance*

Under the optimized conditions, the detection limits of this method were calculated as the concentration corresponding to three times the standard deviation of ten replicate measurements of sample blank solution and were found to be 0.016 and

**Table 2**
Effect of coexisting ions on the MSPE of Cr(III) ($C_{Cr(III)}=1$ μg L$^{-1}$) and total Cr ($C_{Total\ Cr}=1$ μg L$^{-1}$).

| Co-existing ions | Tolerance limit of ions for Cr (III) (mg L$^{-1}$) | Tolerance limit of ions for total Cr (mg L$^{-1}$) |
|---|---|---|
| $Na^+$ | 1000 | 1000 |
| $K^+$ | 1000 | 1000 |
| $Ca^{2+}$ | 1000 | 1000 |
| $Mg^{2+}$ | 1000 | 1000 |
| $Cu^{2+}$ | 10 | 10 |
| $Co^{2+}$ | 10 | 10 |
| $Zn^{2+}$ | 10 | 10 |
| $Ni^{2+}$ | 10 | 5 |
| $Cd^{2+}$ | 10 | 5 |
| $Mn^{2+}$ | 2.5 | 2.5 |
| $Ba^{2+}$ | 2.5 | 2.5 |
| $Al^{3+}$ | 2.5 | 2.5 |
| $Pb^{2+}$ | 1 | 1 |

**Table 3**
Determination of certified reference material (mean ± sd, $n=3$).

| CRM | Certified (μg $mL^{-1}$) | Founded (μg $mL^{-1}$) | | |
|---|---|---|---|---|
| | | Cr (III) | Cr (VI) | Total Cr |
| GBW08607 | 0.517 ± 0.010 | 0.503 ± 0.014 | Not found | 0.506 ± 0.018 |
| GBW08607 (Oxidation) | | Not found | 0.498 ± 0.019 | 0.498 ± 0.019 |

**Table 4**
Analytical results for Cr(III) and Cr (VI) in water samples (mean ± sd, $n=3$).

| Species | Xuanwu Lake water | | | Tap water | | |
|---|---|---|---|---|---|---|
| | Spiked (μg $L^{-1}$) | Found (μg $L^{-1}$) | Recovery (%) | Spiked (μg $L^{-1}$) | Found (μg $L^{-1}$) | Recovery (%) |
| Cr(III) | 0 | 0.070 ± 0.003 | / | 0 | 0.0540 ± 0.003 | / |
| | 0.050 | 0.130 ± 0.005 | 108 | 0.100 | 0.140 ± 0.007 | 91 |
| | 0.100 | 0.190 ± 0.006 | 109 | 0.200 | 0.250 ± 0.005 | 98 |
| Cr(VI) | 0 | 0.059 ± 0.007 | / | 0 | 0.066 ± 0.005 | / |
| | 0.100 | 0.140 ± 0.004 | 88 | 0.100 | 0.150 ± 0.002 | 90 |
| | 0.200 | 0.250 ± 0.009 | 97 | 0.200 | 0.290 ± 0.007 | 109 |

0.011 ng $mL^{-1}$, respectively, for Cr(III) and Cr(VI) with the enrichment factors of 100 and 150. The precisions of this method (RSD), examined by seven replicate measurements of 0.1 ng $mL^{-1}$ Cr(III) and 0.1 ng $mL^{-1}$ Cr(VI), were 6.0% and 6.2% respectively, which indicated good reproducibility for the speciation of Cr(III) and Cr (VI). The adsorption capacity is an important factor influencing the performance of the absorbent. The capability study used in this work was based on the method proposed by Maquieira et al. [37], and the maximal adsorption capacity for Cr(III) and Cr(VI) were 9.16 and 18.22 mg $g^{-1}$, respectively.

### 3.7. *Analysis application*

In order to validate the accuracy of proposed procedure, the method was applied for the speciation of Cr(III) and Cr(VI) in certified reference material of GBW08607 environmental water and the results are listed in Table 3. It can be seen that total Cr founded in GBW08607 was 0.506 ± 0.018 μg $mL^{-1}$, which is in good agreement with certified value of 0.517 ± 0.010 μg $mL^{-1}$. Under this condition, these total Cr is mainly existed in Cr(III), but after GBW08607 environmental water was oxidized by hydrogen peroxide in concentrated $NH_3 \bullet H_2O$ medium, total Cr is primary in the form of Cr(VI) and the founded value was 0.498 ± 0.019 μg $mL^{-1}$, which is in excellent agreement with the determined value (0.508 ± 0.012) by SPE using modified SBA-15 mesoporous silica as absorbent coupled with flame atomic absorption spectrometry [38].

To test the applicability of the described method, the developed method was used for the speciation of Cr(III) and Cr(VI) in Xuanwu Lake water and tap water, and the analytical results along with the recoveries by spiking results are given in Table 4. As can be seen, the recoveries of 88–109% were obtained for the spiked samples and these results demonstrated the suitability of presented method for the speciation of Cr(III) and Cr(VI) in environmental samples.

## 4. Conclusions

A novel MSPE method combined with GFAAS was developed for the speciation of Cr(III) and Cr(VI). By contrast with conditional speciation procedure, the proposed Zincon–Si–MNPs based method did not need preliminary reduction and oxidation process, reducing operating error, and is simple, facile and economic for the speciation and preconcentration of chromium. Furthermore, no chelating agent was added in the separation process, preventing the potential transformation of Cr(III) and Cr(VI) and reagent blank.

## Acknowledgments

This work was supported by the National Natural Science Fund of China (90913012, 21275069), Fundamental Research Funds for the Central Universities (KYZ201220), the National Basic Research Program of China (973 program, 2009CB421601, 2011CB911003), Jiangsu Postdoctoral Research Funds (1001002C), the National Science Funds for Creative Research Groups (21121091), and Analysis & Test Fund of Nanjing University.

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