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## ARTICLE

# Simultaneous speciation and determination of arsenic, chromium and cadmium in water samples by high performance liquid chromatography with inductively coupled plasma mass spectrometry

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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The simultaneous separation and determination of As(III), As(V), monomethylarsenic acid (MMA), dimethylarsenic acid (DMA), Cr(III), Cr(VI) and Cd(II) in water samples have been carried out by anion exchange liquid chromatography with inductively coupled plasma mass spectrometry. Ethylenediaminetetraacetic acid was induced to form negatively charged complex with Cr(III) and Cd(II). For achieving the optimum chromatographic conditions, the effect of competing ion type, mobile phase concentration and pH on speciation have been investigated. By compromising among analysis time, chromatographic resolution and sensitivity, 40 mM ammonium nitrate at pH 8.6 as mobile phase has been selected for real sample application. The baseline separation of all the target species has been achieved under isocratic elution. Under the optimized conditions, the limit of detection was in the range 0.07-0.12 µg/L for the various species. The proposed method was applied to determine the target species in surface water and drinking water samples. Arsenate was the dominant arsenic species in all the tested samples. Neither MMA nor DMA was detected in real water samples. The recoveries for spikes of individual species in water sample tested ranged from 88% to 116%.

## Introduction

Trace metal(loid)s are considered to be hazardous for the water environment. The harmful metal(loid)s most likely to be found in contaminated surface water and drinking water are cadmium, chromium and arsenic.<sup>1-3</sup> The major sources of these elements in surface water samples are anthropogenic, such as wastewater from industry, agriculture and opportunity, especially mining wastewater and acid mine drainage (AMD)<sup>4</sup>. The potential toxicity of trace metal(loid)s are strongly determined by the speciation of the elements involved. In natural waters, arsenic occurs predominantly in inorganic forms (arsenite/As(III) and arsenate/As(V)), which are analogous to phosphate making them able to interfere with the essential cellular processes.<sup>5</sup> Besides, the most prominent organoarsenicals being monomethylarsonate (MMA) and dimethylarsinate (DMA) have been reported.<sup>6-8</sup> Chromium exists in two main species of which Cr(III) is considered to be an essential trace element in mammals, while Cr(VI) is thought to increase the incidence of various cancers.<sup>9, 10</sup> The common specie of cadmium in natural samples such as water is Cd(II). Cadmium exposure may result in bioaccumulation in the kidneys and liver<sup>11</sup> and has a close association with the development of diabetes and diabetes-related kidney diseases.<sup>12</sup>

The determination of different species of elements is important for investigating the transformation of elements in

the environmental systems.<sup>13</sup> High performance liquid chromatography (HPLC) coupled to elemental specific detectors, such as inductively coupled plasma mass spectrometry (ICP-MS), has been much used in simultaneous detection and speciation of different elements because of the separation versatility, high sensitivity, element specificity and ease for online coupling.<sup>14</sup> Up to date, ion exchange liquid chromatography (IC)<sup>15-17</sup> and ion-pair reversed-phase chromatography (RP-IPC)<sup>18, 19</sup> are two main chromatographic methods for speciation analysis of trace elements. The most sensitive method is anion-exchange based chromatography ICP-MS, which enables reliable speciation determination in various sample matrices and wide pH range from acidic to alkaline<sup>20</sup>. Generally, due to different sample preservation and analytical procedures, the determination of speciation is performed for the species of each element of interest separately.<sup>18</sup> This would be a complicated and time-consuming process if following such a procedure as speciation of elements one by one. The aim of this work was to develop a method for speciation analysis of the species mentioned above in water samples. The common form of Cd(II) and Cr(III) are cationic in natural water samples. To simultaneously determine all the species in a single chromatographic run with anion-exchange column, complexation with ethylenediaminetetraacetic acid (EDTA) was carried out to form metal-EDTA anionic complex as reported in other works.<sup>21-23</sup>

There are few reports on the simultaneous speciation and detection of metal(loid)s and metal-EDTA complexes using HPLC-ICP-MS<sup>21</sup>. In this paper, the condition for the separation of the target analytes based on isocratic elution has been optimized through balancing analysis time, chromatographic resolution and sensitivity. Isocratic elution needs no equilibration time between samples unlike gradient elution. The matrices interference, sample preservation and stability have been studied. This method has been tested on surface and drinking waters in optimized condition.

## Experimental

### Instrumentation

The HPLC separation was performed with an Agilent series 1200 high performance liquid chromatography system (Tokyo, Japan) equipped with a quaternary pump, an autosampler fitted with a 100  $\mu$ L injection loop, an anion exchange column (Hamilton PRP-X100, 4.1 mm ID  $\times$  250 mm, 10  $\mu$ m) and a guard column (Hamilton PRP-X100, 2.0 mm ID  $\times$  20 mm, 10 $\mu$ m). The column was fully equilibrated before use and all separations were carried out at room temperature varying between 22°C and 27°C. Determination of species after chromatographic separation was performed by an Agilent 7700x ICP-MS (Agilent Corp. USA). The outlet of the chromatographic column was directly connected to a concentric nebulizer of the ICP-MS instrument through PEEK tubing. A nickel sampler and skimmer cones with 1.0 and 0.4 mm orifices, respectively, were used. Data were treated with Agilent MassHunter software and data processing was based on the peak area. The quantification of chromium and arsenic suffers from the polyatomic interferences of carbon and chlorine (e.g. <sup>40</sup>Ar<sup>12</sup>C<sup>+</sup>, <sup>35</sup>Cl<sup>16</sup>O<sup>1</sup>H<sup>+</sup>, <sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup>) on *m/z* 52 and *m/z* 75. In this context, a collision/reaction cell (CRC) was employed to reduce these interferences.<sup>18, 24, 25</sup> The HPLC and ICP-MS operating parameters are given in Table 1. An A&D HR-150AZ analytical balance (Tokyo, Japan) was used for all weighing. An INESA PHS-25 pH meter (Shanghai, China) was employed to determine the pH.

**Table 1** The operating parameters for HPLC and ICP-MS systems

<i>HPLC parameters</i>	
Guard anion exchange column	Hamilton PRP-X100, 2.0 mm ID $\times$ 20 mm, 10 $\mu$ m
Analytical anion exchange column	Hamilton PRP-X100, 4.1 mm ID $\times$ 250 mm, 10 $\mu$ m
Column temperature	Ambient
Mobile phase	40 mM NH <sub>4</sub> NO <sub>3</sub> , pH=8.6
Mobile phase flow	1.0 mL·min <sup>-1</sup>
Typical injection volume	50 $\mu$ L
Elution program	Isocratic
<i>ICP-MS parameters</i>	
Plasma gas flow rate	15.0 L·min <sup>-1</sup>
Auxiliary gas flow rate	0.90 L·min <sup>-1</sup>
Plasma RF power	1550 W
Carrier gas	1.05 L·min <sup>-1</sup>
Collision gas and flow rate	He, 3.9 mL·min <sup>-1</sup>
Monitored ion	<sup>52</sup> Cr, <sup>53</sup> Cr, <sup>75</sup> As, <sup>111</sup> Cd
Dwell time/isotope	0.5s (Cd, Cr), 1.0s (As)

### Standards and reagents

Nitric acid (HNO<sub>3</sub>,  $\geq$ 99.999% metals basis), ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, semiconductor grade), ammonium dihydrogen phosphate (NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>,  $\geq$ 99.99% metals basis), diammonium hydrogen phosphate ((NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>,  $\geq$ 99.99%

metals basis) and disodium ethylenediaminetetraacetic acid (EDTA,  $\geq$ 99.99% metals basis) were purchased from Aladdin Reagent Co. Ltd., Shanghai, China. The ultrapure deionized water (18.2 M $\Omega$  cm, Beijing Purkinje General Instrument Co. Ltd) was used for preparing all standards and solutions including mobile phase. Stock solution of 1,000 mg/L As(III) and As(V) were obtained from O2SI smart solutions (Charleston, USA). The 1000 mg/L stock solution of MMA and DMA were prepared by dissolving methylarsonic acid mono sodium salt hydrate and cacodylic acid sodium salt (Dr. Ehrenstorfer, Ausberg, Germany) in deionized water, respectively. The 1,000 mg/L stock solution of Cr(VI), Cr(III) and Cd(II) were prepared by dissolving appropriate amount of potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>), chromic chloride (CrCl<sub>3</sub>·6H<sub>2</sub>O) and cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) (AR, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) in 1% nitric acid, respectively. All intermediate stock solutions were prepared daily by appropriate dilution of stock solutions in deionized water at room temperature.

### Mobile phase preparation

For optimizing the HPLC separation condition, mobile phases of various compositions were prepared by dissolution of the appropriate amount of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>/NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> or HNO<sub>3</sub> in deionized water and pH adjusted with NH<sub>3</sub>·H<sub>2</sub>O. The mobile phases were freshly prepared and filtered through a 0.45  $\mu$ m cellulose acetate membrane filter (Shanghai, China) then degassed in an ultrasonic bath prior to use.

### Complexation of metal-EDTA

Although the complexing method of EDTA is an effective separation procedure for metal elements, lack of selectivity leads to the difficulty of determination of trace elements in environmental samples with complicated matrices. As a strong chelating agent, EDTA is able to form complexes with many major and trace ions present in environmental water, including Al(III), Ba(II), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(II), Fe(III), Mg(II), Mn(II), Ni(II), Pb(II), Sr(II) and Zn(II).<sup>21, 26</sup> And some of the complexes have high stability constants, which will interfere in complexation of target ions. Normally, the concentration of potentially competing ions is subject to a wide natural variability.<sup>26</sup> Therefore, excess EDTA is needed for the treatment of real samples to ensure complete complexation of Cd(II) and Cr(III) in surface and drinking waters and enable metal-EDTA complexes to remain stable during chromatographic separation. An EDTA concentration of 3 mM was considered adequate for the complexing and applied for treatment of standard solutions and real water samples.<sup>23</sup> The complexation of cations with EDTA for standard solutions was achieved by adding the appropriate amounts of Cr(III), Cd(II), EDTA and phosphate buffer pH adjusted to 7 into a 15 mL glass tube, then incubating in a water bath set to at 70°C for 15 min to ensure the formation of metal-EDTA complex with the great efficiency.<sup>22, 23</sup>

### Sample collection and analysis

Surface water samples (named SW1 to SW7) were collected from seven locations of Xiangjiang River in Hunan Province, the south central part of China. The drinking water samples (named TW1 to TW4) came from four water purification plants (No. 1 water plant, No. 2 water plant, No. 8 water plant and Wangcheng water plant) located in Changsha city, the capital of

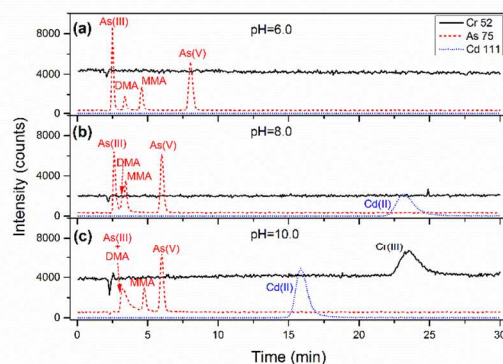
Hunan. The samples collected in 250 mL polyethylene bottles were filtered through a 0.45  $\mu\text{m}$  cellulose acetate membrane filter and separated into two bottles, one with acidification for total elements analysis and the other without acidification to prevent changes in species distribution for speciation. All prepared samples were immediately cooled to 4°C. The analysis was carried out during 24 h after collection.<sup>15</sup> Total elements were determined by ICP-MS under the operating conditions listed in Table 1. Speciation of arsenic, chromium and cadmium were performed by HPLC-ICP-MS. Before analysis, 7.0 mL of each sample in glass vial was diluted with 3.0 mL concentrated ammonium phosphate buffer containing 10 mM EDTA and adjusted pH to 7. The vial was incubated in water bath to allow formation of metal-EDTA complex. The sample matrix was evaluated by spiking 0.5  $\mu\text{g/L}$  of each species and compared to non-spiked samples. The prepared sample was injected into the chromatographic system through a 100  $\mu\text{L}$  loop. The speciation was achieved by isocratic elution and the quantitation was carried out by external calibration.

## Results and Discussion

### Selection of competing ions for chromatographic separation

The retention of element species can be affected by the type of competing anion, the concentration of mobile phase and the solution pH<sup>21</sup>. First, to obtain baseline separation of As(III), As(V), MMA, DMA, Cr(III), Cr(VI) and Cd(II) with a single run, two types of mobile phases were evaluated. For the advantage of strong buffering capacity as well as the ability of varying charge of competing anion (from) by adjusting mobile phase pH, phosphate buffers have been used widely for the speciation of arsenic<sup>27</sup>, selenium<sup>28</sup> and antimony<sup>29</sup>. Mobile phases containing sodium would form deposits upon sampler and skimmer cones of ICP-MS which significantly decrease the plasma stability and ionization efficiency, and cause considerable drift in signal after prolonged use<sup>21</sup>. Therefore, ammonium phosphate was chosen as one of the eluents in this study. Chromatographic separation of As(III), As(V), MMA, DMA, Cr(III), Cr(VI) and Cd(II) was performed by the ammonium phosphate buffers as mobile phase at pH 6.0, 8.0 and 10.0. The results are illustrated in Fig. 1. For chromium species, there was only Cr(III) peak present in the chromatograms. Although the phosphate mobile phase with pH 10 could elute Cr(VI) over 30 min or by promoting flow rate, it would be time consuming and arsenic species could not be separated at the same conditions. Therefore, the ammonium phosphate buffers were not fitted for the speciation of target species. Ammonium nitrate was selected as the other eluent because of its thermal instability (decomposed to gaseous components in ICP torch) to prevent clogging the skimmers<sup>30</sup>, and also because it provides the ionic strength which causes no interference problems in analyte determination<sup>16</sup>. The baseline separation of arsenic and chromium species was achieved at

this condition in 13.5 min using 40 mM ammonium nitrate as mobile phase at pH 8.6 (as shown in Fig. 2(b)).



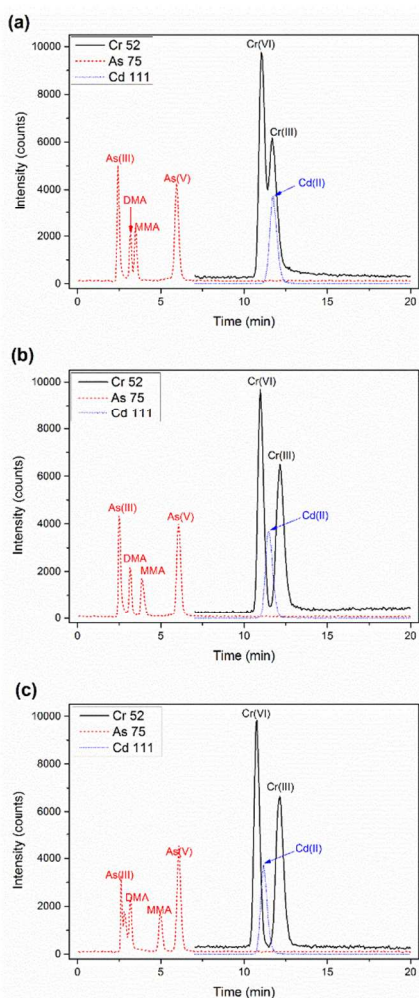
**Fig. 1** Speciation of As, Cr and Cd by 40 mM ammonium phosphate buffers at (a) pH 6.0, (b) pH 8.0, (c) pH 10.0. The mobile phase flow rate was 1.0 mL/min and the concentration of each species was 10  $\mu\text{g/L}$ .

### High-performance liquid chromatography operating conditions and performance

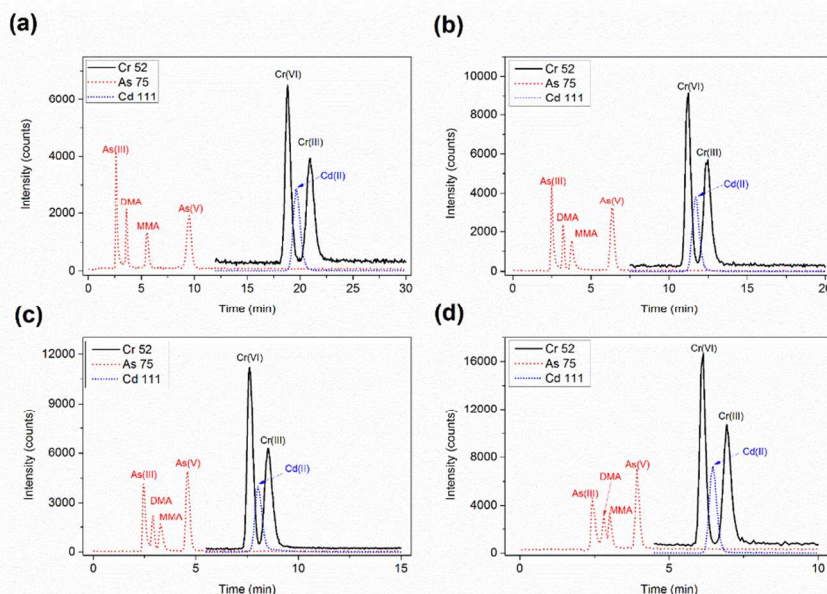
**Effect of the pH value.** Fig. 2 shows the chromatograms of target species separated by ammonium nitrate at different pH values with the other conditions constant (concentration of 40 mM and mobile phase flow rate as 1.0 mL/min). The retention times of target species with different parameters of chromatography were summarized in Table 2. As the competing ion of  $\text{NO}_3^-$  is unaffected by pH, changes of pH value in the mobile phase would not affect the concentration measurement of  $\text{NO}_3^-$ , it means pH of mobile phase would not significantly influence the elution ability of ammonium nitrate<sup>31</sup>. However, the overall negative charge of arsenic species was lowered with pH decreasing, which would shorten their retention times on the anion exchange column<sup>32</sup>. The retention time of arsenic species other than DMA increased when the pH value of mobile phase was adjusted from 8.0 to 9.3. In comparison with ammonium phosphate buffers, the intensity of arsenic species decreased with ammonium nitrate as mobile phase. This could be ascribed to a sensitivity improvement in the plasma excitation conditions using phosphate buffers<sup>33</sup>. According to acid dissociation constant of chromic acid, Cr(VI) mainly exists in aqueous solution as chromate ( $\text{CrO}_4^{2-}$ ) at  $\text{pH} \geq 8$ <sup>34</sup>. Therefore, the retention time of Cr(VI) did not change obviously when the mobile phase pH increased from 8.0 to 9.3. Although the formation of  $[\text{Cr}(\text{EDTA})]^-$  has been confirmed by ESI-MS<sup>31</sup>, the characteristic and stability of the complex have not been studied very well. As demonstrated in Fig. 2, the retention time of Cr(III) reduced with decreasing pH and the overlap of chromium peaks was observed at pH 8.0 (Fig. 2(a)). The baseline separation of arsenic and chromium species was achieved at pH 8.6 as shown in Fig. 2(b). Thus, the optimal pH value for the mobile phase was 8.6.

**Table 2** Effect of pH value and competing ion concentration on retention time of As, Cr and Cd species using ammonium nitrate as mobile phase.

Parameters of chromatography		Retention time (min)								
Concentration of $\text{NH}_4\text{NO}_3$ (mM)	pH value of solution	As(III)	DMA	MMA	As(V)	Cr(VI)	Cr(III)	Cd(II)		
40	8.0	2.44	3.18	3.49	5.96	11.06	11.71	11.75		
40	8.6	2.52	3.17	3.90	6.08	11.00	12.17	11.5		
40	9.3	2.64	3.18	4.98	6.09	10.87	12.14	11.19		
30	8.6	2.64	3.61	5.55	9.51	18.85	20.97	19.68		
40	8.6	2.50	3.23	3.79	6.36	11.00	12.17	11.50		
50	8.6	2.47	2.90	3.30	4.60	7.64	8.54	8.03		
60	8.6	2.45	2.81	3.02	3.94	6.12	6.95	6.47		



**Fig. 2** Speciation of As, Cr and Cd by 40 mM ammonium nitrate at (a) pH 8.0, (b) pH 8.6, (c) pH 9.3. The mobile phase flow rate was 1.0 mL/min and the concentration of each species was 10  $\mu\text{g/L}$ .



**Fig. 3** Speciation of As, Cr and Cd by (a) 30 mM, (b) 40 mM, (c) 50 mM, (d) 60 mM ammonium nitrate at pH 8.6. The mobile phase flow rate was 1.0 mL/min and the concentration of each species was 10  $\mu\text{g/L}$ .

**Effect of the competing ions concentration.** Chromatographic separation of chromium species was performed when the  $\text{NH}_4\text{NO}_3$  concentration varied from 30 to 60 mM with the other conditions constant (pH at 8.6 and mobile phase flow rate as 1.0 mL/min). The chromatographic results are demonstrated in Fig. 3. As the concentration of  $\text{NH}_4\text{NO}_3$  increased, the total separation time reduced from around 23 to 8 min. Also, the resolutions of arsenic species were damaged while increasing the concentration of competing ion. With increasing the concentration from 30 to 60 mM, the resolutions of DMA and MMA declined sharply from 4.94 to 1.02. When the concentration exceeded 40 mM, the arsenic species could not be separated in baseline. Therefore, the concentration of 40 mM was chosen as a compromise among rapid analysis, high resolution and sensitivity.

#### Analytical performance characteristics

Under the optimized conditions, a series of standard solutions in the range 0.1-10.0  $\mu\text{g/L}$  for arsenic, chromium and cadmium species were measured. Calibration curves for quantification were obtained by plotting the peak area versus the concentration of corresponding target specie. The correlation coefficients obtained after linear regression were greater than 0.999. The detection limits calculated on the basis of three times of the standard deviations of the blank signals ( $S/N=3$ ,  $n=9$ ) ranged from 0.07 to 0.12  $\mu\text{g/L}$  for all target species. The reproducibility from multiple injections ( $n=9$ ) of a mixed standard solution containing 0.5  $\mu\text{g/L}$  of each target species showed that the relative standard deviations of As(III), As(V), MMA, DMA, Cr(III), Cr(VI) and Cd(II) were 6.2%, 2.9%, 4.1%, 7.4%, 4.4%, 3.6% and 6.8%, respectively. Analytical performance characteristics of the proposed method are summarized in Table 3. The HPLC-ICP-MS method in optimized conditions has been proved the satisfactory precision for the simultaneously speciation of arsenic, chromium and cadmium.

**Table 3** Analytical performance characteristics and application of the proposed HPLC-ICP-MS method.

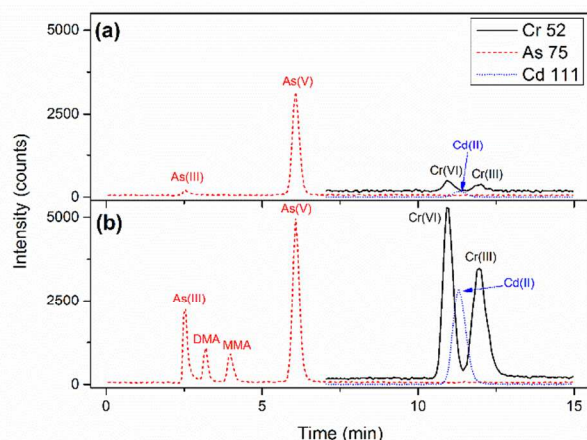
Target species	LOD ( $\mu\text{g/L}$ )	RSD <sup>a</sup>	Drinking water		Surface water	
			Concentration ( $\mu\text{g/L}$ )	Recovery <sup>b</sup> (%)	Concentration ( $\mu\text{g/L}$ )	Recovery <sup>b</sup> (%)
As(III)	0.08	6.2%	0.14-0.35	95-101	0.23-0.75	93-108
As(V)	0.07	2.9%	4.85-7.56	96-99	6.10-15.16	96-100
MMA	0.08	4.1%	N.D.	89-94	N.D.	90-93
DMA	0.11	7.4%	N.D.	88-101	N.D.	93-105
Cr(III)	0.10	4.4%	0.27-0.64	92-98	0.23-0.57	91-97
Cr(VI)	0.07	3.6%	0.23-0.69	94-99	0.25-0.60	93-102
Cd(II)	0.12	6.8%	0.25-0.42	102-115	0.38-1.05	105-116

<sup>a</sup> The mixed standard solution containing 0.5  $\mu\text{g/L}$  of each target species

<sup>b</sup> Spiked 5.0  $\mu\text{g/L}$  for each target species

### Application of the method to real water samples

The proposed method was applied to the simultaneous determination of As(III), As(V), MMA, DMA, Cr(VI), Cr(III) and Cd(II) in 11 real water samples, 7 surface water samples from Xiangjiang River and 4 tap water samples from water plants in Changsha, China. The results were shown in Table 3. Neither MMA nor DMA was detected in any water samples. Arsenate was the dominant arsenic species at concentrations of 6.10-15.16  $\mu\text{g/L}$  and 4.85-7.56  $\mu\text{g/L}$  in surface water and tap water, respectively. Arsenite was detected in all real water samples at concentrations lower than 0.8  $\mu\text{g/L}$ . The total arsenic concentrations in surface water samples were a bit higher than tap water. Chromium existed in all samples at concentrations from 0.48 to 1.33  $\mu\text{g/L}$  and the ratios of Cr(VI) to Cr(III) were close to 1:1. Recovery was tested in water samples spiked of 5.0  $\mu\text{g/L}$  arsenic, chromium and cadmium standards. Fig. 4 shows the typical chromatograms from surface water sample with and without spiked. The recoveries for each individual species were ranged from 88% to 116%. Column recoveries were in the range from 88% to 95%, from 92% to 103% and from 95% to 108% for arsenic, chromium and cadmium, respectively.



**Fig. 4** Typical chromatograms from (a) surface water sample and (b) spiked sample with 5.0  $\mu\text{g/L}$  each standard solutions.

### Conclusions

Anion exchange liquid chromatography coupled with ICP-MS was used for the simultaneous speciation of As(III), As(V), MMA, DMA, Cr(III), Cr(VI) and Cd(II) in water. Ammonium phosphate buffer and ammonium nitrate have been selected as potential mobile phase for speciation. Although ammonium phosphate buffer has been used widely in arsenic speciation, it could not separate all the species of arsenic and chromium at

the same condition and it would be time consuming for simultaneous speciation. The effect of competing ion concentration and pH value of ammonium nitrate as mobile phase on separation of target species has been investigated. The baseline separation of all the target species has been achieved by 40 mM ammonium nitrate as mobile phase at pH 8.6 using isocratic elution. Under the optimized conditions, the detection limits were ranged from 0.07  $\mu\text{g/L}$  to 0.12  $\mu\text{g/L}$  for all the target species. The proposed method was verified using drinking water and surface water samples. The recoveries for individual each species ranged from 88% to 116%.

### Acknowledgement

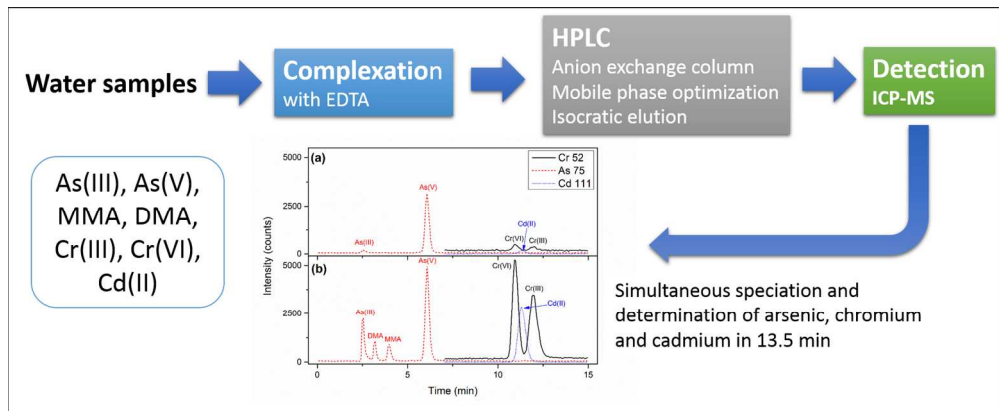
This work was financially supported by National Science and Technology Major Project of China – Water Pollution Control and Treatment (No. 2013ZX07504-001) and National Department Public Benefit Research Foundation of China (No. 201309052).

### Notes and references

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