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The determination of trace amount of Cr(VI) and As(V) in aqueous solution by UV–vis spectrophotometer assisted with preconcentration on a quaternary ammonium ion exchange fiber-in-tube

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ABSTRACT

A simple and sensitive method was developed for the determination of Cr(VI) and As(V) using a microcolumn packed with quaternary ammonium ion exchange fiber for the preconcentration of trace amount of Cr(VI) and As(V) prior to their determination by UV–vis spectrophotometer. It was found that Cr(VI) and As(V) could be almost completely retained on ion-exchange fiber in the pH range of 5.0–6.5 and 3.5–5.0, respectively. With a mixture eluent of 5% (w/v) NH_4Cl and 10% (v/v) NH_3/H_2O solution, they could be almost quantitatively eluted. Under the optimized conditions, the detection limits were $0.2\,\mu g\,L^{-1}$ for Cr(VI) and $0.8\,\mu g\,L^{-1}$ for As(V) with enrichment factors of 96.5 and 95.3, respectively. The relative standard deviations for nine replicate determinations at 5 and $10\,\mu g\,L^{-1}$ for Cr(VI) and As(V) were 2.2 and 3.4%, respectively. These results proved that the proposed method had a potential in the analysis of trace metal ions with good accuracy in real samples.

Keywords: Fiber-in-tube; Cr(VI); As(V); UV spectrometry

1. Introduction

Chromium and arsenic are two toxic elements even at low exposure levels. They are widely distributed in water and air in inorganic forms (Cr (III)/Cr(VI), As (III)/As(V)) and organic forms, causing potentially serious environmental problems for plants, human, and other living organisms [1–3]. Chromium and arsenic entered the body by the drinking water and contaminated food intake and caused increasing risks of cancer in the skin, lungs, liver, kidney, and bladder [4,5]. According to the World Health Organization, the upper permissible level of chromate and arsenate in drinking water is 50 and $10.0\,\mu g\,L^{-1}$, respectively [6]. Consequently, it is of importance to determine the content of Cr(VI) and As(V).

Several modern instrumental techniques, such as atomic fluorescence spectrometry, atomic absorption spectrometry (AAS) [6], inductively coupled plasma atomic emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) [7] and

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UV spectrometry have been applied for the determination of metal elements in various samples. Of all these methods, UV spectrometry is a very attractive option for the determination of trace amount of element in water samples because of its low cost, operational facility and ease for online determination.

However, the direct determination of Cr(VI) and As(V) at extremely low concentration is inaccurate, owing to the concentration of Cr(VI) and As(V) in real sample is close to or below the detection limit of UV–vis spectrophotometer of 4 and 10 $\mu g\,L^{-1}$ [8,9], which restricts its application for direct determination of analytes. Accordingly, an efficient and essential separation/preconcentration procedure is required prior to determination by UV–vis spectrophotometer, leading to higher concentrations and confidence levels of the analytes, resulting in easy determination of the trace elements [10,11].

Solid-phase extraction (SPE) has received an increasing attention for preconcentration of trace analytes due to its rapid phase separation, simple operation, lower organic solvent consumption and possibility of combination with different analytical techniques [12–15]. Adsorbent material played a key role for SPE, which determined the sensitivity and selectivity of the analytical method. Various adsorbents, including active carbon [16], alumina [17], functionalized silica gel [18], biological adsorbent [4,19], ion-exchange resin [2], ion-exchange fiber [20,21], have been applied as adsorption materials in SPE for the separation and preconcentration of metal ions from environmental water. Among these adsorbents, ion-exchange fiber has drawn growing attention because of its high specific surface area, rapid diffusion speed, high chemical stability, and high sorption capacity [22].

Consequently, a simple preconcentration technique using a fiber-in-tube microcolumn prior to determination of trace Cr(VI) and As(V) by UV–vis spectrophotometer was developed. Experimental parameters affecting the adsorption and elution of the analytes, such as pH of the sample, flow rate and volume, eluent and interfering ions were investigated.

2. Experimental

2.1. Apparatus

The concentration of Cr(VI) and As(V) were determined at 540 nm and 450 nm, respectively, using a double-beam UV–vis spectrophotometer (model TU-1901, Beijing, China) [24]. The pH values of solutions were controlled with a pH meter (Shanghai Leici Co. Ltd., Shanghai, China) supplied with a combination electrode. Polyethylene microcolumn with a 2 mm inner diameter and 2.5 cm length (Tianjin 9th Plastic Factory, Tianjin, China) were employed for the fiber-in-tube microextraction.

2.2. Standard solution and reagents

The stock standard solutions containing 100 mg L^{-1} Cr(VI) was obtained from the National Institute of Standards (Beijing, China). As(V) standard solution (100 mg L^{-1}) was prepared by dissolving appropriate amounts of $Na_2HAsO_4{\cdot}7H_2O$ (A.R., The First Reagent Factory of Shanghai, Shanghai, China) in deionized water. Working standard solutions were prepared by diluting standard solutions to appropriate concentrations. Ultrapure grade sulfuric acid and hydrochloric acid were used to prepare 2.5 $mol\,L^{-1}$ sulfuric acid and hydrochloric acid (11% (v/v)) for sample acidification. The 1,5-diphenylcarbazide (DPC) solution for Cr(VI) was prepared by dissolving 0.5 g of DPC in 100 mL of acetone and water (1:1), which was stored in a brown glass bottle at 4°C. The developer solution for As(V) was prepared with 5 mL L-Ascorbic acid (5% (w/v)), 5 mL ammonium molybdate (3% (w/v)), 2.5 mL antimony potassium tartrate hemihydrate (0.56% (w/v)) and 12.5 mL sulfuric acid (2.5 $mol\,L^{-1}$).

The pH values of solutions were achieved by adding hydrochloric acid or sodium hydroxide to the solution. All solvents and sample solutes were of analytical grade and purchased from Tianjin Kermel chemical reagent Co., Ltd. (Tianjin, China). The grafted polypropylene materials made by our laboratory were cleaned by soaking them with 2.0 $mol\,L^{-1}$ nitric acid for about 12 h. All containers were cleaned with deionized water.

2.3. Microcolumn preparation

To prepare the extraction tube, approximately 25 mg of ion-exchange fibers (diameter: 20 μm; special surface area: 3.1 $m^2\,g^{-1}$; ion-exchange capacity: 3.2 $mmol\,g^{-1}$) [23] were packed into a PE preconcentration tube that was 2.5 cm length and had a 2 mm inner diameter. Before its use, 2.0 $mol\,L^{-1}$ nitric acid solution and doubly deionized water passed through the column to clean it.

2.4. General procedure

A portion of aqueous sample solution containing the analytes was prepared, and the pH value was adjusted to the desired value with sodium hydroxide

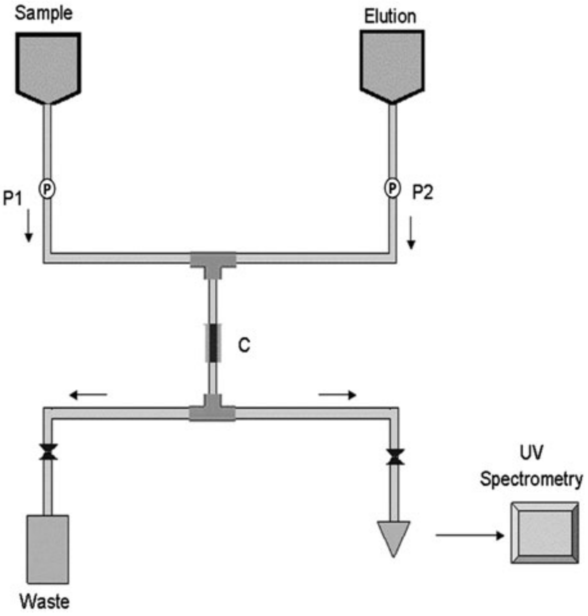

Fig. 1. The operation for preconcentration/separation and determination of Cr(VI) and As(V). C, fiber in microcolum; P1 and P2, switch.

of $0.1\,\mathrm{mol\,L^{-1}}$ and hydrochloric acid of $0.1\,\mathrm{mol\,L^{-1}}$. The solutions were passed through the microcolumn at a flow rate of $3.0\,\mathrm{mL\,min^{-1}}$, unless otherwise specified. The retained metal ions were subsequently eluted with 1.0 mL of 5% (w/v) NH_4Cl and 10% (v/v) NH_3/H_2O solution. The analytes in the elution solution were determined by UV–vis spectrophotometer.

The experimental setup is showed in Fig. 1. In separation/preconcentration step, pump P1 was activated, sample solution was passed through the microcolumn and Cr(VI) and As(V) were retained on the fibers, waste solution was effluent from the tube. In elution step, pump P2 was activated, the eluent was propelled through the microcolumn and the eluting solution was determined with UV–vis spectrophotometer. After that, doubly deionized water was passed through the microcolumn to wash off the residual until the solution was neutral for the next use.

3. Results and discussion

The quaternary ammonium ion-exchange fiber carries positive charge, which can interact with negative charge [24]. The mechanism is as follows:

$$\mathrm{R-N^+(CH_3)_3 + A^- \Leftrightarrow R-N(CH_3)_3A}$$

Arsenic and chromium mainly exist in anion forms ($HCrO_4^-$, CrO_4^{2-}, $Cr_2O_7^{2-}$, $H_2AsO_4^-$ and $HAsO_4^{2-}$) in aqueous solution, and hence, Cr(VI) and As(V) species could adsorb onto the surface of quaternary ammonium adsorbent [25].

3.1. Effect of pH

The pH value played an essential role in the sorption of Cr(VI) and As(V) on the fibers. In order to evaluate the effect of pH, 10 points of pH values of the samples were selected from 1.0 to 10.0, the space of the each point is 1.0. The adsorption percentage was calculated based on the difference between the amounts of Cr(VI) and As(V) in the origin sample and the waste solution.

The results in Fig. 2 indicated that the adsorption percentage for Cr(VI) was maintained at about 95% in the pH ranging from 5.0 to 6.5 and then decreased as the pH increased.

Amines on the quaternary ammonium ion-exchange fibers can provide positive charge. Consequently, the following chemical reaction would occur on the surface of the fibers in the high alkaline medium:

$$\mathrm{R-N^+(CH_3)_3 + OH^- \Leftrightarrow R-N(CH_3)OH}$$

With the increase in pH the degree of fiber dissociation decreased, which resulted in the decrease of the number of the positive charge. When the number of positive charge decreased, the adsorption capacity of the fiber decreased sharply. When $pH < 7$, $HCrO_4^-$ is predominant in the solution. One exchange site on the fiber was required for the adsorption. In contrast, CrO_4^{2-} became the main specie in solutions at $pH > 7$,

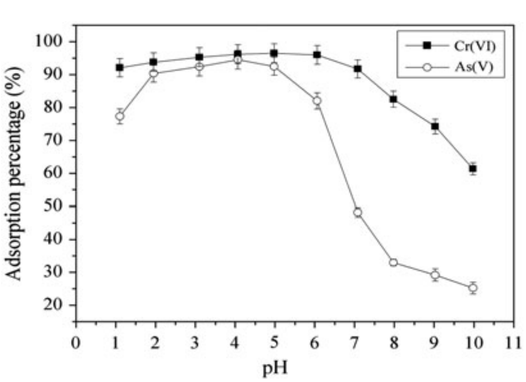

Fig. 2. Effect of pH on the adsorption percentage of Cr(VI) and As(V). Conditions: concentration of Cr(VI): $500\,\mathrm{\mu g\,L^{-1}}$; concentration of As(V): $800\,\mathrm{\mu g\,L^{-1}}$, sample volume, 25 mL.

which need two exchange sites on fiber for the adsorption. Therefore, with the increase in pH (pH > 7), the adsorption capacity decreased [25].

As for As(V) solutions, its protonated form of H_3AsO_4 are expected to exist primarily at a lower pH. At pH 3–5, the form of $H_2AsO_4^-$ is presented predominantly, which required one exchange site on the fiber for the adsorption. In addition, $HAsO_4^{2-}$ dominates at pH > 5.0 and need two exchange sites on fiber for the adsorption [26]. Therefore, there was a decrease in adsorption percentage at higher pH values.

3.2. *Effect of sample flow rate*

The flow rate of the sample solution affected the adsorption capacity and contact time between Cr(VI) and As(V) species and the fiber-in-tube microcolumn [27]. Therefore, the sample flow rate should be optimized. The results in Fig. 3 showed that the adsorption percentages of Cr(VI) (>96%) and As(V) (>95%) were almost unchanged in the flow rate range of 1.0–3.0 mL min^{-1}, while it decreased when the flow rate was above 3 mL min^{-1}. These findings implied inadequate sorption capacity of the fiber-in-tube microcolumn or contact time between two phases, while the flow rate was higher than 3 mL min^{-1}.

3.3. *Optimization of elution conditions*

3.3.1. *Choice of eluent*

The type and concentration of eluent were important factors on desorption of the analytes from the fibers. A suitable eluent should effectively elute the analytes from the fiber-in-tube microcolumn with small volume. From Fig. 2, it was clearly shown that few Cr(VI) and As(V) were adsorbed on the fibers in high alkaline medium. Consequently, various concentrations of sodium hydroxide and weak base were studied for desorption of the retained Cr(VI) and As (V) on the fibers. As seen in Table 1, it was obvious that NH_3/H_2O was better than NaOH, and the eluent system of NH_4Cl and NH_3/H_2O solution was sufficient for the recovery of Cr(VI) and As(V) (>95%). The phenomenon could be explained that a large number of OH^- replaced the adsorption sites of anion because of the competition adsorption. In addition, the decreased dissociation degree of the quaternary ammonium ion exchange fiber in the high alkaline medium resulted in the decreasing of adsorption capacity of the fiber.

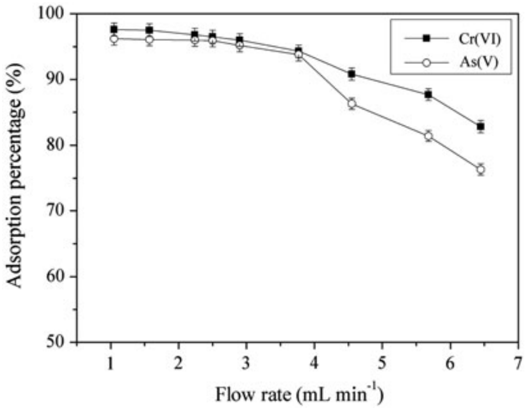

Fig. 3. Effect of flow rate on the adsorption of Cr(VI) and As(V). Conditions: concentration of Cr(VI): 500 μg L^{-1}; concentration of As(V): 800 μg L^{-1}; sample volume: 25 mL.

3.3.2. *Concentration of NH_3/H_2O*

Various concentrations of NH_3/H_2O (0–20%) (v/v) were studied to determine the optimum eluent concentration. The results in Fig. 4 showed that Cr(VI) and As(V) could be eluted quantitatively with 10% (v/v) NH_3/H_2O solution. Therefore, a mixture eluent of 5% (w/v) NH_4Cl and 10% (v/v) NH_3/H_2O solution was selected. The mixture eluent was made by 2.5 mg NH_4Cl and 5 mL 22.4% (w/v) NH_3/H_2O in 45 mL doubly deionized water.

3.3.3. *Eluent flow rate*

The effect of elution flow rate on the recovery of target analytes was examined with the flow rate in the range of 0.25–6.0 mL min^{-1}. The results indicated that the analytes could be recovered quantitatively when the

Table 1
Effect of eluent on the desorption of Cr(VI) and As(V)

Eluent	Eluent volume (mL)	Recovery (%)	
		Cr(VI)	As(V)
NaOH (1 mol/L)	1	74.3(2.5)	80.4(2.3)
	2	85.4(3.1)	87.1(2.7)
NaOH (2 mol/L)	1	64.2(3.1)	76.7(2.1)
	2	77.8(2.3)	81.6(1.9)
5% (w/w)NH_4Cl	1	65.6(2.5)	60.4(1.8)
10% (v/v) $NH_3.H_2O$	1	91.2(2.5)	88.2(2.7)
	2	92.4(2.4)	92.3(2.2)
$NH_3.H_2O^-$ NH_4Cl	1	96.4(2.8)	95.1(1.6)

Notes: values in the parentheses are RSD (N = 3).
$C_{Cr(VI)}$: 3.2 μg L^{-1}, $C_{As(V)}$: 10.0 μg L^{-1}.

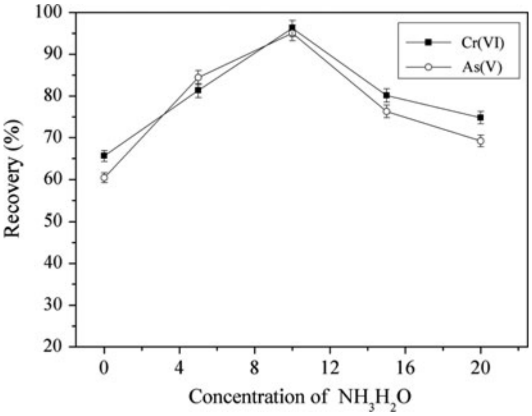

Fig. 4. Effect of concentration of NH_3/H_2O on recovery (%) of Cr(VI) and As(V). Conditions: concentration of Cr(VI): $3.2\,\mu g\,L^{-1}$; concentration of As(V): $10\,\mu g\,L^{-1}$, sample volume: 100 mL; sample flow rate: $3.0\,mL\,min^{-1}$; eluent volume: 1.0 mL; elution flow rate: $0.5\,mL\,min^{-1}$.

elution flow rate was in the range of $0.25–0.5\,mL\,min^{-1}$. The recovery decreased obviously with a further increase in the elution flow rate. In the present study, elution flow rate of $0.5\,mL\,min^{-1}$ was selected in order to shorten the analysis time.

3.3.4. Eluent volume

Different volumes of the eluent in the range of 0.25–2.0 mL were passed through the microcolumn and determined by UV–vis spectrophotometer. The results in Fig. 5 demonstrated that the recovery increased as the eluent volume increased in the range of 0.25–1.0 mL. Cr(VI) and As(V) could be recovered quantitatively at a flow rate of $1.0–2.0\,mL\,min^{-1}$(>95%). The findings implied adequate desorption capacity with 1.0 mL of mixed eluents. Therefore, 1.0 mL of 5% (w/v) NH_4Cl and 10% (v/v) NH_3/H_2O solution was used.

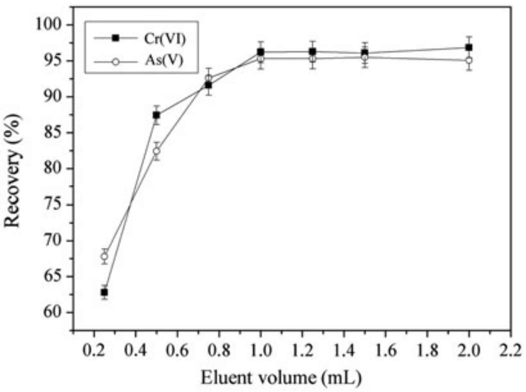

Fig. 5. Effect of eluent volume on recovery (%) of Cr(VI) and As(V). Conditions: concentration of Cr(VI), concentration of As(V): $10\,\mu g\,L^{-1}$; sample flow rate: $3\,mL\,min^{-1}$; elution flow rate: $0.5\,mL\,min^{-1}$.

3.4. Sample volume

In order to achieve a high preconcentration factor from a sample with low analyte concentration, a large volume of sample solution is required. Consequently, samples with volumes of 50, 100, 150, 200, and 250 mL containing $3.2\,\mu g\,L^{-1}$ of Cr(VI) and $10\,\mu g\,L^{-1}$ As (V) were adsorbed, respectively. The experimental results showed that quantitative recoveries for Cr(VI) and As (V) were obtained when sample volume was less than 150 mL, the adsorbed Cr(VI) and As(V) could be eluted with 1.0 mL eluent. In this work, 100 mL sample volume was used for the analysis of samples.

3.5. Detection of Cr(VI) and As(V)

The determination of Cr(VI) and As(V) in drinking water was performed under the optimum experimental conditions. The results were 16.82 ± 1.23 ($n = 3$) and 1.21 ± 0.11 ($n = 3$) for Cr(VI) and As(V), respectively. The accuracy of the method was investigated through the recovery from spiked samples. The produced recoveries were 97.2 and 102.4%, respectively.

3.6. Column reuse

In order to evaluate the performance of the microcolumn, under the optimal condition, 100 mL of Cr(VI) and As(V) solutions and 1 mL eluent were continuously passed through one fiber-in-tube microcolumn, and the analytes in the eluents were determined by UV–vis spectrophotometer. It was showed that the column could be reused for at least five times without significant decrease in the determination of Cr(VI) and As(V) in Table 2. The recoveries of As(V) decreased

Table 2
Number of times the fiber-in-tube microcolumn was re-used

Times	Recovery (%)	
	Cr(VI) ($3.2\,\mu g\,L^{-1}$)	As(V) ($10\,\mu g\,L^{-1}$)
1	97.5 ± 2.1	96.2 ± 1.3
5	96.4 ± 1.8	95.1 ± 1.6
10	94.6 ± 2.5	93.1 ± 1.7
15	92.9 ± 2.2	91.4 ± 2.1

after five times perhaps because a little analytes was retained the column [15].

3.7. Effect of interfering ions

The interference caused by potential present in water samples, such as Cl^-, SO_4^{2-}, PO_4^{3-} and HCO_3^-, was studied using 1 mL samples containing 20 μg L^{-1} of Cr(VI) and As(V) each. The tolerance limits of interfering ions were listed in Table 3. The experimental results showed that recovery of the target analytes remained above 94% even in the presence of ions in the following concentrations: 1,000 μg L^{-1} of Cl^-, SO_4^{2-}, PO_4^{3-} and the mixture of Cl^-, SO_4^{2-} for As(V); 1,000 μg L^{-1} of PO_4^{3-}, 5,000 μg L^{-1} of Cl^-, SO_4^{2-} and the mixture of Cl^-, SO_4^{2-}, PO_4^{3-}, HCO_3^-, for Cr(VI).

It can be explained that the adsorption sites of the fiber had no fully occupied even in the concentration of 1,000 μg L^{-1} for interfering ions, and therefore, a large number of adsorption sites is available. The results indicated that the proposed method could be applied in real sample analysis.

3.8. Detection limits and precision

Under the optimized operating conditions, the calibration curve for Cr(VI) and As(V) were linear in the concentration range of 0.2–50.0 μg L^{-1} and 0.8–50.0 μg L^{-1}, respectively. The corresponding regression equations and determination coefficients (R^2) of the method for Cr(VI) and As(V) was $y = 0.0574X + 0.0043$ ($R^2 = 0.9992$) and $y = 0.0161X + 0.005$($R^2 = 0.9988$), respectively. The relative standard deviations (RSD) of Cr(VI) and As(V) were 2.2% ($C = 5$ μg L^{-1}, $n = 9$) and 3.4% ($C = 10$ μg L^{-1}, $n = 9$), respectively. Using a volume of 100 ml of aqueous solution of Cr(VI) and As(V), the obtained limits of detection were 0.2 and 0.8 μg L^{-1} with enrichment factors of 96.5 and 95.3, respectively.

Table 3
Tolerance concentration of interfering ions

Interferent ions (μg L^{-1})	Cr(VI) Recovery (%)			As(V) Recovery (%)		
	1,000	5,000	25,000	1,000	5,000	25,000
Cl^-	97.5 ± 2.2	95.2 ± 1.8	91.6 ± 2.5	95.5 ± 1.9	92.2 ± 1.8	89.6 ± 2.5
SO_4^{2-}	98.7 ± 1.7	96.9 ± 2.3	94.7 ± 1.7	94.7 ± 2.2	92.9 ± 2.7	87.2 ± 2.6
PO_4^{3-}	94.2 ± 2.6	91.2 ± 2.2	77.5 ± 2.3	94.3 ± 2.6	90.6 ± 2.5	71.5 ± 2.3
Cl^- SO_4^{2-} $PO_4^{3-}$$HCO_3^-$	101.1 ± 2.4	94.3 ± 2.3	84.5 ± 2.5	95.1 ± 2.4	91.3 ± 2.8	76.5 ± 2.9

Conditions: concentration of Cr(VI), As(V), 20 μg L^{-1}; sample volume, 100 mL; eluent volume: 1.0 mL; sample flow rate: 3 mL min^{-1}; eluent flow rate: 0.5 mL min^{-1}.

Table 4
Comparison of the published methods with the proposed method in this work

Adsorbent	Detection method	Enhancement factor	Detection limit (μg L^{-1})		Refs.
			Cr(VI)	As(V)	
Animal fibers	FAAS	32[a]	0.3		[7]
Diaion HP-2MG	ETAAS	10[a]	0.03		[30]
Mesoporous Al_2O_3	ICP-MS	5/5[b]	0.018	0.007	[31]
Amberlite XAD-4 resin	UV–vis	27[a]	6		[16]
Multiwalled carbon nanotubes	FAAS	100[a]	0.9		[27]
Mesoporous TiO2	ICP-OES	50[b]		0.49	[28]
Carbon nanofibers	ICP-MS	33[b]		0.24	[8]
Activated alumina	AAS	10[b]		2	[32]
Silica	ICP-OES	26.7[b]		0.15	[29]
Fiber	UV–vis	96.4[a]/95.3[b]	0.2	0.8	This work

[a]Enrichment factor of Cr(VI), [b]Enrichment factor of As(V).

The method was compared with a variety of methods reported recently in the literature for the preconcentration and determination of Cr(VI) and As(V). It can be seen From Table 4, the limit of detection of this method for Cr(VI) was lower than those obtained by FAAS [6,26] and UV–vis [15]. The detection limit for As(V) of this work was at the same level with ICP-OES [27,28].

4. Conclusions

In the present paper, a new method using fiber-in-tube online coupled with UV–vis spectrophotometer was applied for the determination trace amounts of Cr(VI) and As(V). The detection limits were 0.2 and $0.8\,\mu\text{g L}^{-1}$ with enrichment factors of 96.5 and 95.3 for Cr(VI) and As(V), respectively. The proposed method was simple and rapid, with high sensitivity, good accuracy, and reproducibility. Therefore, the method was expected to have great potential in the analysis of Cr(VI) and As(V) in various samples especially in remote regions.

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