

# Multiwalled carbon nanotubes for speciation of chromium in environmental samples

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Received 3 December 2006; received in revised form 21 December 2006; accepted 22 December 2006

Available online 4 January 2007

## Abstract

A solid phase extraction procedure has been established for chromium speciation in natural water samples. The procedure is based on the solid phase extraction of the Cr(VI)-ammonium pyrrolidine dithiocarbamate (APDC) chelate on multiwalled carbon nanotubes (MWNTs). After oxidation of Cr(III) to Cr(VI) by using hydrogen peroxide, the presented method was applied to the determination of the total chromium. The level of Cr(III) is calculated by difference of total chromium and Cr(VI) levels. The procedure was optimized for some analytical parameters including pH, eluent type, flow rates of sample and eluent, matrix effects, etc. The detection limit based on  $3\sigma$  criterion was  $0.90 \mu\text{g L}^{-1}$  for Cr(VI). The adsorption capacity of multiwalled carbon nanotubes was  $9.50 \text{ mg g}^{-1}$  Cr (VI). The presented method was applied for the speciation of chromium in natural water sample with satisfactory results (recoveries  $> 95\%$ , R.S.D.'s  $< 9\%$ ).

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**Keywords:** Multiwalled carbon nanotubes; Speciation; Chromium; Solid phase extraction; Atomic absorption spectrometry

## 1. Introduction

Trace metals are one of the major pollutants in the environment [1–3]. There are two types of heavy metal sources namely natural and man-made [4]. The major sources of these heavy metals in the environmental samples are man-made such as soils and dusts from traffic, industry and weathered materials. Trace metals are useful indicators of contamination in surface soil environments by man-made emission sources [5–7]. Among heavy metal pollutants, chromium plays a major role in polluting environment [8]. Investigation on chromium contamination is also an important part of analytical chemistry, due to importance of the chromium species on the human health [8–11]. Chromium exists in Cr(III) and Cr(VI) oxidation states in aqueous solutions. The properties of these species are different [12]. Trivalent chromium, the main chemical form found in foods, is essential for maintaining normal glucose metabolism [13]. Cr(VI) oxidation state is detrimental to health as it may be involved in the

pathogenesis of some diseases like liver, kidney, lung and gastrointestinal cancers [14]. Chromium species are major water pollutants, usually as a result of some industrial pollution including tanning factories, steel works, industrial electroplating, wood preservation, etc. and artificial fertilizers [15–18].

The determination of chromium species is not possible directly by instrumental methods including flame and/or graphite furnace atomic absorption spectrometry. To solve this problem generally separation–preconcentration procedures including liquid–liquid extraction, ion-exchange, electroanalytical techniques, membrane filtration, cloud point extraction and solid phase extraction [19–26] have been used prior to the determination of chromium species by flame and/or graphite furnace atomic absorption spectrometry. The speciation procedures for chromium by are generally based on the preconcentration–separation of one of the chromium species (Cr(III) or Cr(VI)). In these procedures, total chromium was determined after the reduction of Cr(VI) or by the oxidation of Cr(III) according to bases of the procedure. Especially solid phase extraction is very important place in the speciation studies of chromium. Various new solid phase extraction materials have been suggested for chromium speciation. At this point, carbon nanotubes (CNTs) have been proposed as a

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novel solid phase extractor for various inorganic and organic materials at trace levels [27–33]. CNTs are one of the most commonly used building blocks of nanotechnology. With 100 times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they seem to be a very interesting material [28,34]. CNTs can be visualized as a sheet of graphite that has been rolled into a tube, and divided into multiwalled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs) according to the carbon atom layers in the wall of the nanotubes [31–34].

The aim of the presented work is to establish a speciation procedure based on adsorption of Cr(VI)-APDC chelates on MWNTs for chromium in natural water samples.

## 2. Experimental

### 2.1. Instruments

A Perkin-Elmer AAnalyst 700 atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air-acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer. A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase.

### 2.2. Reagents and solutions

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Deionised water (Milli-Q Millipore  $18.2 \text{ M}\Omega \text{ cm}^{-1}$  conductivity) was used for all dilutions. All the plastic and glassware were cleaned by soaking in dilute  $\text{HNO}_3$  (1+9) and were rinsed with distilled water prior to use. Multiwalled carbon nanotube (Aldrich No.: 636630) was purchased from Aldrich, Milwaukee, WI, USA. An ammonium pyrrolidine dithiocarbamate (APDC) solution (0.1%, w/v) was prepared by dissolving the requisite amounts of APDC in water/ethanol (75%/25%, v/v). The solution was discharged 1 day. Hydrogen peroxide solution (3%, w/v) was prepared in dilute sodium hydroxide solution (pH 10).

The element standard solutions used for calibration were produced by diluting a stock solution of  $1000 \text{ mg L}^{-1}$  of the given element supplied by Sigma–Aldrich. Stock solutions of diverse elements were prepared from high purity compounds. The calibration standards were not submitted to the preconcentration procedure.

Phosphate buffer solutions ( $\text{H}_2\text{PO}_4^-/\text{H}_3\text{PO}_4$ ) were prepared by mixing of appropriate volumes of  $1 \text{ mol L}^{-1}$  sodium dihydrogen phosphate and phosphoric acid solutions for pH 2–3. Acetate buffer solutions ( $\text{CH}_3\text{COO}^-/\text{CH}_3\text{COOH}$ ) were prepared by mixing of appropriate volumes of  $0.1 \text{ mol L}^{-1}$  acetic acid and  $0.1 \text{ mol L}^{-1}$  sodium acetate solutions for pH 4 and 6. For pH 7, a 250 mL of borate buffer was prepared by use of 2.5 mL of

$1 \text{ mol L}^{-1}$  HCl and 0.445 g  $\text{NaBO}_2$ . Ammonium buffer solutions ( $\text{NH}_4^+/\text{NH}_3$ ) were prepared by mixing of appropriate amounts of  $0.1 \text{ mol L}^{-1}$  ammonia and  $0.1 \text{ mol L}^{-1}$  ammonium chloride solutions for pH 8–9.

### 2.3. Column preparation

Three hundred milligrams of MWNTs was loaded after washing with acetone,  $1 \text{ mol L}^{-1}$   $\text{HNO}_3$  solution and water, respectively, into a  $10 \text{ mm} \times 100 \text{ mm}$  glass column with a glass frit resin support. The resin bed was approximately 1.5 cm. The column was preconditioned by the blank solution prior to each use. After the elution, the resin in the column was washed with a 10–15 ml of the eluting solution and of water, subsequently.

### 2.4. Test procedure

Ten millilitres of buffer solution (to give the desired pH between 2 and 9) and 2.0 mg of APDC solution were added to 40 mL of solution containing  $20 \mu\text{g}$  of chromium(VI). The column was preconditioned by passing buffer solution. Cr(VI)-APDC solution was passed through the multiwalled carbon nanotube column at a flow rate of  $5 \text{ mL min}^{-1}$ . After passing of this solution, the column was rinsed twice with 10 mL of water. The adsorbed chelate on the nanotube was eluted with 10 mL portion of  $1 \text{ mol L}^{-1}$  nitric acid in acetone. The eluent was evaporated over a hot plate to near dryness. The residue was diluted to 5 mL with distilled water. The eluent was analysed for the determination of chromium(VI) concentrations by an atomic absorption spectrometry.

Oxidation of Cr(III) to Cr(VI) has been performed by using the procedure given in literature [35,36]. After adjustment of the pH of the solution pH 10, 10 mL of 3% hydrogen peroxide was added. The solution was heated at  $80^\circ\text{C}$  for 40 min. Then the solution was boiled for 10 min in order to remove any excess of  $\text{H}_2\text{O}_2$ . Then test procedure given above was applied to this solution. Chromium was determined by FAAS.

After oxidation of Cr(III) to Cr(VI) by using  $\text{H}_2\text{O}_2$  in basic media, the method was applied to the determination of the total chromium. The level of Cr(III) is calculated by difference of total chromium and Cr(VI) concentrations.

### 2.5. Application to natural waters

Water samples analysed were filtered through a cellulose membrane filter (Millipore) of  $0.45 \mu\text{m}$  pore size. The pH of the samples was adjusted to 2.0 with buffer solution. Then the procedure given above was applied. The levels of chromium in the samples were determined by flame atomic absorption spectrometry.

Total chromium in natural water samples was determined as chromium(VI) after oxidation of chromium(III) to chromium(VI) in the natural waters. The oxidation of Cr(III) to Cr(VI) was performed by the procedure given in literature [35,36].

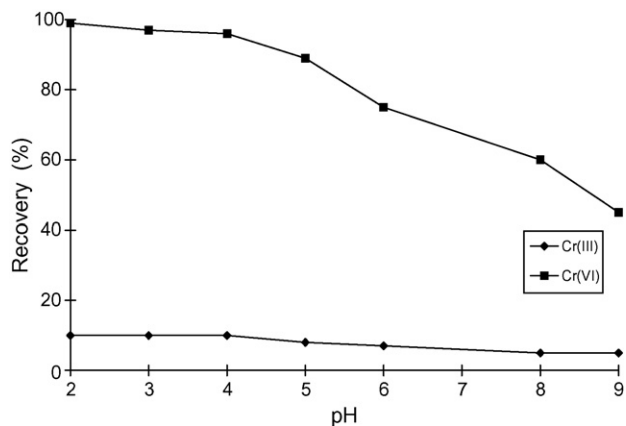


Fig. 1. Influences of pH on the recoveries of Cr(III) and Cr(VI) on MWCNTs,  $N=3$ .

### 3. Results and discussion

#### 3.1. Effects of pH

The influences of pH of the working media on the recoveries both Cr(III) and Cr(VI) on multiwalled carbon nanotube were investigated in the pH range of 2–9. The results are depicted in Fig. 1. The recovery values for chromium(III) were below 10% all the investigated pHs. Chromium(VI) was recovered quantitatively in the pH range of 2–4 as APDC chelates. These results show that the speciation of chromium(III) and chromium(VI) is possible at pH range of 2–4. All further works are carried out at pH 2 for speciation of chromium species.

#### 3.2. Effects of amounts of ammonium pyrrolidine dithiocarbamate

APDC is a well-characterised reagent that reacts with over 30 metal ions to form very stable complexes [37,38]. APDC gives also stable complexes with Cr(VI) [37,38]. APDC has been continuously used on the preconcentration–separation studies by the various researchers due to its properties. The effects of amount of ammonium pyrrolidine dithiocarbamate on the recoveries of Cr(VI) on MWNTs were also investigated. The results are depicted in Fig. 2. The recovery of chromium(VI) on nanotubes was not quantitative without APDC. The recovery values increased with the increasing amounts of APDC. After 1 mg of APDC, the recovery values were quantitative. Further studies were carried out with 2 mg of APDC.

#### 3.3. Influences of the eluent

The influences of various eluents given in Fig. 3 on the recovery of retained Cr(VI) on multiwalled carbon nanotubes were also studied at the optimal working conditions. For these studies 10 mL of each eluents were used. Quantitative recovery value for Cr(VI) was obtained only with 1 mol L<sup>-1</sup> nitric acid in acetone.

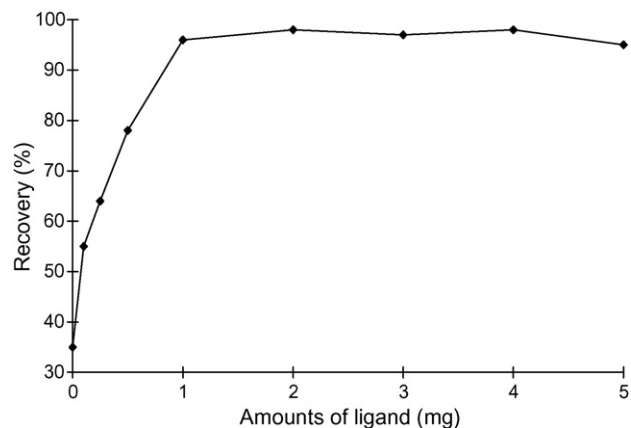


Fig. 2. Effects of amount of APDC on the recoveries of Cr(VI) on multiwalled carbon nanotubes (MWNTs),  $N=3$ .

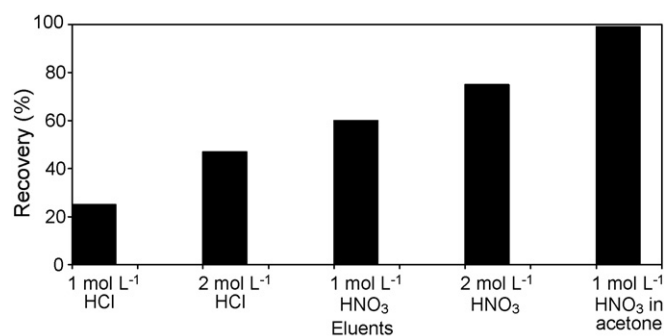


Fig. 3. Effect of various eluents on the recoveries of Cr(VI),  $N=3$ .

#### 3.4. Flow rates of sample and eluent

It is expected that sample solutions can be passed through the multiwalled carbon nanotubes column at a higher flow rate without sacrificing the recoveries of analytes because a large volume of sample solution is needed in the separation–preconcentration procedures. The influences of the flow rate of the sample and eluent solutions on the recoveries of Cr(VI) was examined in the range of 1.0–10.0 mL min<sup>-1</sup>. The results are given in Fig. 4. The flow rate of the sample and eluent solutions had no obvi-

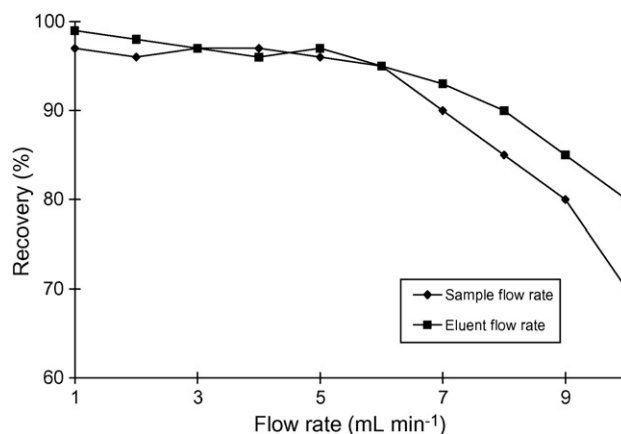


Fig. 4. Influences of flow rates on the recoveries of Cr(VI) on multiwalled carbon nanotubes,  $N=3$ .

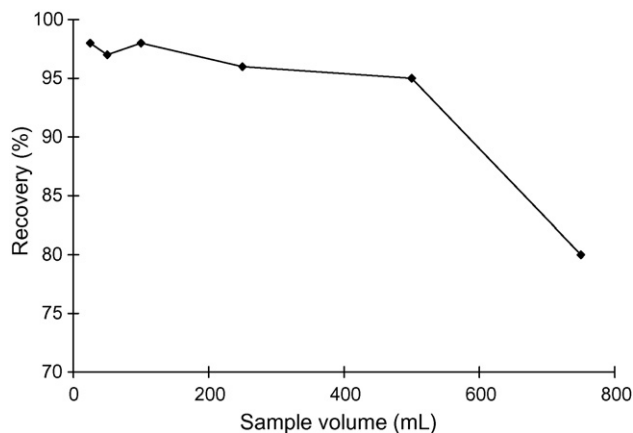


Fig. 5. Influences of sample volume on the recoveries of Cr(VI),  $N=3$ .

ous influence on the quantitative recoveries of chromium(VI) at the range of 1.0–6.0 mL min<sup>-1</sup>. Five millilitres per minute was chosen as the flow rate of the sample and eluent solutions in subsequent experiments.

### 3.5. Sample volume

The influences of sample volume on the retention behaviors of Cr(VI)-APDC chelates on the multiwalled carbon nanotubes column was studied by varying the sample volume from 25 to 750 mL. The results for this study are depicted in Fig. 5. Cr(VI)-APDC chelates were quantitatively recovered in the sample volume range of 25–500 mL. After 500 mL, the recovery values for chromium(VI) were not quantitative. The recoveries of Cr(VI) decrease probably due to the excess analytes loaded over the capacity of nanotubes with increasing sample volume above 500 mL. The highest preconcentration factor was 100, when the final volume was 5 mL.

### 3.6. Effect of diverse ions

Various salts and metal ions were added individually to a solution containing Cr(VI) and the test procedure given in Section 2 was applied. The tolerance limit was set, as the diverse ion amount require causing  $\pm 5\%$  error in the determination of Cr(VI). The results obtained are given in Table 1. Under these optimized conditions, most of the probable concomitant cations and anions remained in the first phase. The tolerable levels of some heavy metal ions are suitable for the separation and preconcentration of chromium(VI) in the real samples examined in

Table 1

Influences of some foreign ions on the recoveries of chromium(VI) ( $N=3$ )

Ion	Added as	Concentration (mg L <sup>-1</sup> )	Recovery (%)
Na <sup>+</sup>	NaCl	20,000	96 ± 2 <sup>a</sup>
K <sup>+</sup>	KCl	5,000	97 ± 3
Ca <sup>2+</sup>	CaCl <sub>2</sub>	5,000	96 ± 2
Mg <sup>2+</sup>	MgCl <sub>2</sub>	5,000	95 ± 3
Cl <sup>-</sup>	NaCl	30,000	96 ± 2
F <sup>-</sup>	NaF	1,000	95 ± 2
NO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	3,000	95 ± 2
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	3,000	96 ± 3
PO <sub>4</sub> <sup>3-</sup>	Na <sub>3</sub> PO <sub>4</sub>	3,000	96 ± 3
CH <sub>3</sub> COO <sup>-</sup>	CH <sub>3</sub> COONa	1,000	95 ± 2
HCO <sub>3</sub> <sup>-</sup>	NaHCO <sub>3</sub>	1,000	96 ± 2
Al <sup>3+</sup>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	100	95 ± 3
Cd <sup>2+</sup>	CdSO <sub>4</sub>	100	96 ± 2
Mn <sup>2+</sup>	MnSO <sub>4</sub>	100	96 ± 3
Zn <sup>2+</sup>	ZnSO <sub>4</sub>	100	97 ± 2
Ni <sup>2+</sup>	NiSO <sub>4</sub>	100	96 ± 3
Fe <sup>3+</sup>	FeCl <sub>3</sub>	100	95 ± 2
Cu <sup>2+</sup>	CuSO <sub>4</sub>	100	98 ± 2
Pb <sup>2+</sup>	PbSO <sub>4</sub>	100	95 ± 2
Co <sup>2+</sup>	CoSO <sub>4</sub>	100	96 ± 2
Cr <sup>3+</sup>	Cr(NO <sub>3</sub> ) <sub>3</sub>	250	96 ± 3

<sup>a</sup> Mean  $\pm$  standard deviation.

the present study, because of the levels of transition metals in these samples are lower than their interferic level.

### 3.7. Capacity of multiwalled carbon nanotubes

0.1 g multiwalled carbon nanotubes was added to 50 mL of solution containing 1.0 mg of Cr(VI) at pH 2.0. After shaking for 30 min, the mixture was filtered to study the adsorption capacity of nanotubes. Ten millilitre of the supernatant solution was diluted to 100 mL and determined by flame atomic absorption spectrometry. The capacity of MWNTs for Cr(VI) was 9.50 mg g<sup>-1</sup>.

### 3.8. Determination of total chromium

In order to determine total chromium, firstly, model solutions that contain different amounts Cr(VI) and Cr(III) were prepared. Then Cr(III) ions in the model solutions were oxidized to Cr(VI) by using H<sub>2</sub>O<sub>2</sub> in basic media [35,36]. Because of the quantitative recoveries for Cr(VI) were obtained at pH 2.0, the pH of the basic solution was adjusted to pH 2.0 by the addition of buffer solution. Then the procedure given in Section 2 was applied to these solutions. The results are given in Table 2. The results show

Table 2  
Total chromium determinations in spiked test solutions (volume: 100 mL,  $N=4$ )

Added ( $\mu$ g)		Found ( $\mu$ g)			Recovery (%) <sup>a</sup>			Relative error (%)		R.S.D. (%)	
Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
0	25	–	24.3 ± 0.5	24.3 ± 0.5	–	97 ± 1	97 ± 1	–	–2.9	–	2.1
10	15	9.8 ± 0.4	14.4 ± 0.6	24.2 ± 0.5	98 ± 2	96 ± 2	97 ± 2	–2.0	–4.2	4.1	4.2
15	10	14.6 ± 0.7	9.9 ± 0.3	24.5 ± 0.6	97 ± 2	99 ± 1	98 ± 2	–2.7	–1.0	4.8	3.0
25	0	24.6 ± 0.8	–	24.6 ± 0.8	98 ± 2	–	98 ± 2	–1.6	–	3.3	–

<sup>a</sup> Mean  $\pm$  standard deviation.

Table 3  
Speciation of Cr(III) and Cr(VI) and total chromium in some natural and waste water samples<sup>a</sup> (sample volume: 100 mL,  $N=4$ )

Samples	Added ( $\mu\text{g}$ )		Found ( $\mu\text{g}$ )			Recovery (%)			Relative error (%)		R.S.D. (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Total Cr	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
River water	–	–	$1.6 \pm 0.1$	$1.1 \pm 0.1$	$2.7 \pm 0.2$	–	–	–	–	–	6.3	9.1
	5.0	5.0	$6.4 \pm 0.3$	$5.9 \pm 0.2$	$12.3 \pm 0.4$	$97 \pm 1$	$97 \pm 1$	$97 \pm 1$	–3.1	–3.4	4.7	3.4
	10.0	5.0	$11.1 \pm 0.6$	$5.8 \pm 0.3$	$16.9 \pm 0.6$	$96 \pm 2$	$95 \pm 2$	$95 \pm 2$	–4.5	–5.2	5.4	5.2
	5.0	10.0	$6.5 \pm 0.3$	$10.8 \pm 0.5$	$17.3 \pm 0.5$	$98 \pm 2$	$97 \pm 2$	$98 \pm 2$	–1.5	–2.8	4.6	4.6
Waste water	–	–	$8.5 \pm 0.4$	$5.2 \pm 0.2$	$13.7 \pm 0.5$	–	–	–	–	–	4.7	3.8
	5.0	10.0	$13.1 \pm 0.6$	$14.9 \pm 0.7$	$28.0 \pm 0.8$	$97 \pm 2$	$98 \pm 2$	$98 \pm 2$	–3.1	–2.0	4.6	4.7
	10.0	5.0	$18.2 \pm 0.7$	$9.8 \pm 0.4$	$28.0 \pm 0.7$	$98 \pm 2$	$96 \pm 2$	$98 \pm 2$	–1.6	–4.1	3.8	4.1
	10.0	10.0	$18.1 \pm 0.8$	$14.6 \pm 0.7$	$32.7 \pm 0.9$	$98 \pm 2$	$96 \pm 2$	$97 \pm 2$	–2.2	–4.1	4.4	4.8
Tannery waste water	–	–	$12.7 \pm 0.9$	$9.4 \pm 0.5$	$22.1 \pm 0.9$	–	–	–	–	–	7.1	5.3
	10.0	10.0	$21.9 \pm 0.7$	$19.1 \pm 0.6$	$41.0 \pm 0.8$	$96 \pm 1$	$98 \pm 1$	$97 \pm 1$	–3.7	–1.6	3.2	3.1
	10.0	20.0	$22.1 \pm 0.5$	$28.7 \pm 0.9$	$50.8 \pm 1.5$	$97 \pm 1$	$98 \pm 2$	$98 \pm 2$	–2.7	–2.4	2.3	3.1
	20.0	10.0	$31.6 \pm 0.8$	$18.8 \pm 0.7$	$50.4 \pm 0.9$	$97 \pm 1$	$97 \pm 1$	$97 \pm 1$	–3.5	–3.2	2.5	3.7

<sup>a</sup> Mean  $\pm$  standard deviation.

that the proposed method could be applied for the determination of total chromium.

### 3.9. Figure of merits

The detection limit (LOD) of the present work was calculated under optimal experimental conditions after application of the preconcentration procedure to blank solutions. The limit of detection for chromium(VI) based on three times the standard deviations of the blank ( $k=3$ ,  $N=21$ ) was  $0.90 \mu\text{g L}^{-1}$ .

The precision of the determination of chromium(VI) was evaluated under the optimum conditions mentioned above for the presented procedure. The procedure was repeated 10 times for chromium(VI). It was found that the recovery of Cr(VI) was  $96 \pm 3$  at 95% confidence level.

### 3.10. Applications

We have explored feasibility of presented speciation procedure on multiwalled carbon nanotubes for the determination of Cr(III), Cr(VI) and total chromium in natural waters including river water from Green River-Tokat, waste water from Tokat and tannery waste water from industry in Tokat City. The preconcentration–speciation procedure was applied to the determination of chromium species by standard addition method. The reliability was checked by spiking experiments. The results are presented in Table 3. The recovery of spiked samples was satisfactorily reasonable and was confirmed using addition method, which indicates the capability of the solid phase extraction system in the speciation of chromium in natural water samples.

Table 4  
Comparative data from some recent studies on Cr(III) and Cr(VI) speciation

Technique	System	Media	Detection system	PF	DL ( $\mu\text{g L}^{-1}$ )	R.S.D. (%)	Reference
SPE	Cr(III)-dithizone and reduction of Cr(VI)	Chromosorb 108	FAAS	71	0.75	<9	[17]
SPE	Cr(VI)-DPC and oxidation of Cr(III)	Polysorb C-18	Spectrophotometry	12	2.4	1.3	[18]
SPE	Cr(VI) and Cr(III)-alumina	Activated alumina column	FAAS	–	0.45	<9	[25]
SPE	Cr(VI)-ADPC and oxidation of Cr(III)	Amborsorb 563	FAAS	125	2.70	<9	[35]
CPE	Cr(III)-1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one and reduction of Cr(VI)	Triton X-100	ICP-AES	20	0.81	3.2	[39]
Coprecipitation	Cr(VI)-ethyl xanthate complex and oxidation of Cr(III)	–	FAAS	100	0.5	3.1	[40]
SPE	Cr(III) and Cr(VI)-APDC	LiChrospher 100 RP-8 and LiChrospher 60 RP-18	HPLC-UV Detection	–	0.2	2	[41]
SPE	Cr(III) and reduction of Cr(VI)	<i>Bacillus sphaericus</i> loaded Diaion SP-850	FAAS	50	0.50	<5	[42]
SPE	Cr(VI)-ADPC and oxidation of Cr(III)	Multiwalled carbon nanotube	FAAS	100	0.90	<9	Present work

CPE, cloud point extraction; SPE, solid phase extraction; PF, preconcentration factor; DL, detection limit.



#### 4. Conclusion

A speciation procedure for chromium species on multiwalled carbon nanotubes in natural water samples was presented. The procedure was successfully applied to speciation of chromium species of various natural water samples. The comparative data from some recent studies on chromium speciation are given in Table 4. The optimal conditions are comparable for the procedure in the literature with quantitative recovery values and lower detection limit for chromium speciation. The multiwalled carbon nanotubes speciation procedure is superior to those reported chromium separation–preconcentration methods in term of selectivity, detection limit, applicable pH range, capacity, no need to consumption of organic solvents and enrichment factor.

#### Acknowledgements

The authors are also grateful for the financial support of the Unit of the Scientific Research Projects of Gaziosmanpasa University and the Unit of the Scientific Research Projects of Erciyes University. Authors thank Mrs. K.O. Saygi for her help.

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