

Full Length Research Paper

# Solid phase extraction and determination of Chromium species using multiwalled carbon nanotubes by solid phase extraction: Flame atomic absorption spectrometry (FAAS)

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Accepted 8 March, 2013

**Multiwalled carbon nanotubes (MWNTs) were used as absorbent for extraction of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)), ions in the presence of diethyldithiocarbamate as a chelate by solid phase extraction method. A novel and selective method for the fast determination of trace amounts of chromium species in water samples has been developed. The procedure is based on the selective formation of chromium diethyldithiocarbamate complexes at different pH in the presence of Mn(II) as an enhancement agent of chromium signals followed by elution with organic eluents and determination by atomic absorption spectrometry. The maximum capacity of the employed disks was found to be  $498 \pm 3 \mu\text{g}$  and  $487 \pm 2 \mu\text{g}$  for Cr(III) and Cr(VI), respectively. The detection limit of the proposed method is 21 and 12  $\text{ng}\cdot\text{L}^{-1}$  for Cr(III) and Cr(VI), respectively. The proposed method was successfully applied for determination of chromium Species Cr(III) and Cr(VI) in different water samples.**

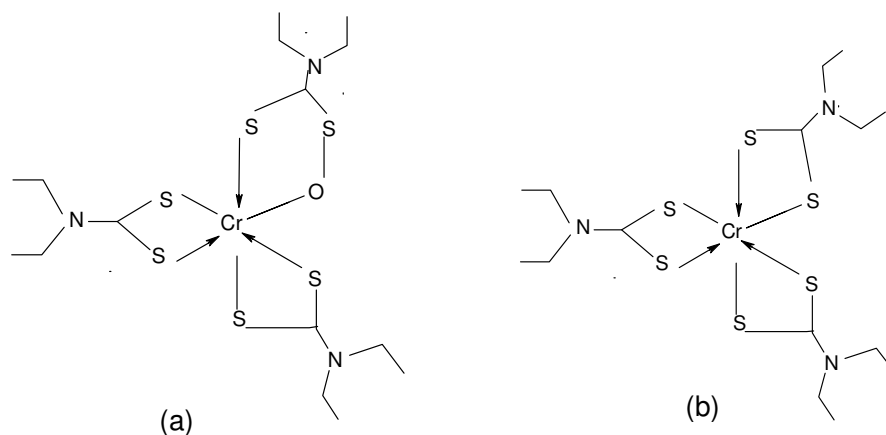
**Key words:** Solid phase extraction, sodium diethyldithiocarbamate, flame atomic absorption spectrometry, Octadecyl silica membrane disk, multiwalled carbon nanotubes (MWNTs).

## INTRODUCTION

Toxicological studies have proved that the degree of toxicity of an element directly depends on the species in which it is present. The direct determination of trace metals especially toxic metal ions such as Cr(III), tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden et al., 1976a; Takeshima et al., 1969; Taylor et al., 1995). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest (Jones et al., 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar et al., 1998; Caroli et al., 1991). The application

of solid phase extraction technique for pre-concentration of trace metals from different samples results in several advantages such as minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form (Alexandrova and Arpadjan, 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan et al., 1997); filter paper (Leyden et al., 1975); cellulose (Gennaro et al., 1983) and ion exchange resins (Grote and Kettrup, 1985). Silica gel, alumina, magnesia and zirconia are the major



**Figure 1.** (a) Cr(III) and Na-DDTC tris [diethyldithioato-S,S']- Cr(III). (b) Reaction product of Cr(VI) and Na-DDTC bis[diethyldithioato-S,S']-[ diethyl-per-oxydithioato,O,S]- Cr(III).

inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger, 1979), of which silica gel is the most widely used solid support due to the well documented thermal, chemical and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau and Cooper, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek et al., 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening et al., 1991; Moghimi, 2013).

Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on chemical bond formation between the silica gel surface groups and those of the organic modifier; and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger, 1979). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, 1997a, b; Tong et al., 1990; Dadler et al., 1987).

The most successful selective solid phases for soft metal ions are sulfur-containing compounds, which are widely used in different analytical fields. Amongst these sulfur-containing compounds are dithiocarbamate derivatives for selective extraction of Cr(III) (Mahmoud, 1998, 1999) and pre-concentration of various cations (Leyden et al., 1976b; Narin et al., 2000; Akama et al., 2000; Ohta et al., 2001; Cuculic et al., 1997; Moghimi et al., 2009; Moghimi, 2008; Tehrani et al., 2005; Thurman and Mills, 1998; Pawliszyn, 1997; Izatt et al., 1996;

Hagen et al., 1990; Krueger and Fild, 1995; Yamini and Ashraf-Khorassani, 1994; Shamsipur et al., 1999; 2001; Brunner et al., 2003; Zelder et al., 2005; Boll et al., 2005; Nayebi and Moghimi, 2006; Moghimi et al., 2006; Moghimi, 2007) 2-mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng et al., 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova and Arpadjan, 1993). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi and Tajodini, 2010). Sorption of Cr(III) by some sulfur containing complexing agents loaded on various solid supports (Tajodini and Moghimi, 2010), was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of silver(I), Cr(III) and palladium(II) (Moghimi et al., 2009); 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin et al., 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros et al., 1998) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin et al., 2000) are also sulfur containing silica gel phases, with chelating agent such as Natriumdiethyldithiocarbaminat (Na-DDTC), Cr(III) and Cr(VI) can form different complexes (Figure 1a and b). As a result of the reaction of Cr(III) and Na-DDTC, one product can be found tris [diethyldithioato-S,S'] - Cr(III). Cr(VI) is reduced by dithiocarbamates to Cr(III) which leads to two different chromium complexes.

In the case of Na-DDTC, these compounds are (bis[diethyldithioato-S,S']-[diethyl-per-oxydithioato,O,S]-Cr(III) (Hope et al., 1977; Andrlé et al., 1997; Alfassi and Wai, 1990).

**Table 1.** Instrumental parameters for chromium determination.

Parameters	Chromium
Hollow cathode lamp current (mA)	7.0
Wavelength (nm)	357.9
Silt width (nm)	0.2
Background correction	BC off
Measurement mode	Integrate
Air flow rate (L.min <sup>-1</sup> )	13.50
Acetylene flow rate (L.min <sup>-1</sup> )	2.90

The aim of this work was to develop a simple, highly sensitive and efficient method for the selective extraction and concentration of trace amounts of Cr(III) and Cr(VI) ions from aqueous media by means of pH adjustment using multiwalled carbon with octadecyl silica membrane disks nanotubes.

The present article describes the preconcentration of DDTc complexes of Cr(III) and Cr(VI) on octadecyl silica disk and their determination by off-line flame atomic absorption spectrometry (FAAS).

## EXPERIMENTAL

### Reagents, standard and sample solutions

All reagents were of analytical Merck grade. Na-DDTC (0.1%w/v) was prepared in deionized water. Organic eluents used were of High-performance liquid chromatography (HPLC) grade. Standard solutions of Cr(III) and Cr(VI) were prepared by appropriate dilution of 1000 µg.mL of stock solutions made from chromium(III), chloride and potassium dichromate, respectively.

Acidic buffer (pH=4,5) was prepared by mixing 100,200g CH<sub>3</sub>COONa.2H<sub>2</sub>O and 150,30 ml HOAc glacial in 1 L distilled water, respectively. The 0.45 mm nitro-cellulose membrane filters used for the wastewater samples filtration, were obtained from Schleicher and Schuell, Germany (REF-NO: 10404012) and 47 mm diameter solid phase extraction disks used for extraction and preconcentration of chromium from waste water samples, were supplied by Supelco ENVI-DISK (Cat.NO.57171). Multiwalled carbon nanotube (Plasma Chem GmbH) was purchased from Plasma, Rudower Chaussee 29, and D-12489 Berlin.

### Apparatus

A Varian SpectrAA model 200 atomic-absorption spectrometer was used for chromium ions determinations. The operational characteristics of employed parameters are summarized in Table 1. A Metrohm model 691 digital pH meter equipped with a combined glass-calomel electrode was used for pH adjustments and a Millipore filtration set for solid phase extraction.

### Proposed procedure

150 mg of multiwalled carbon nanotubes was loaded after washing with acetone, 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution and water, respectively, into

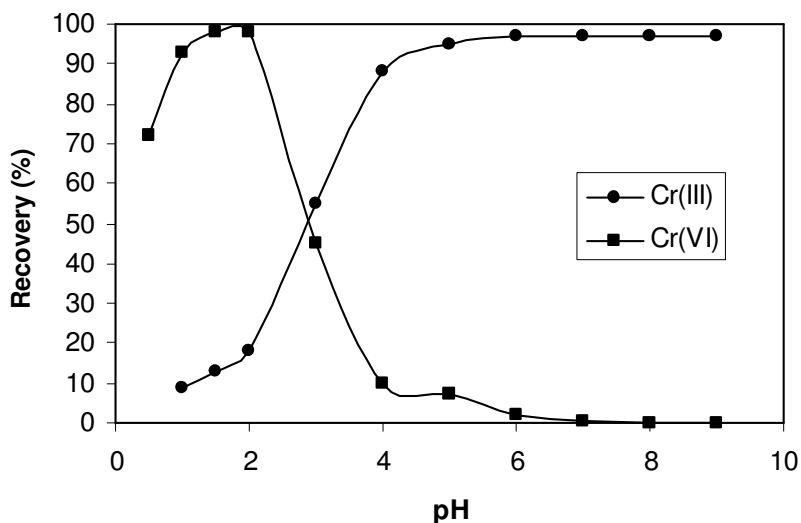
an ENVI-DISK<sup>TM</sup> (47 mm diameter and 0.5 mm thick) containing octadecyl-bonded silica (80 µm Particles, 6 nm Pore size). Extraction was performed of multiwalled carbon nanotubes with ENVI-DISK<sup>TM</sup> (47 mm diameter and 0.5 mm thick) containing octadecyl-bonded silica (80 µm Particles, 6 nm Pore size). Typical capacity of a disk for satisfactory retention of compounds ranges from 10 to 20 mg. The disks were used in conjunction with a standard Millipore 47 mm filtration apparatus connected to a desktop vacuum pump. In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be performed before its use. Thus, after placing the disk in the filtration apparatus, 10 ml of methanol was poured onto the disk and immediately drawn through it by applying a slight vacuum. After all of the solvent had passed through the disk, it was dried by passing air through it for a few minutes. The disk conditioning started by pouring 10 ml of methanol onto the disk. Immediately a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reached the surface of the disk. The disk was not allowed to dry. This is to ensure complete wetting of the disk with the organic solvent. It is preferable to leave extra methanol above the disk rather than to allow get in contact with the disk surface. Immediately thereafter, 20 ml of water was introduced onto the disk and was drawn through it. The disk was then dried under vacuum for 5 min or longer if necessary. This is especially important for the disks which are used for the first time. This step pre-wets the surface of disk prior to the extraction of Cr(III) and Cr(VI) ions from water. Then, a sample solution containing Cr(III) and Cr(VI), species while its pH was adjusted to 1.5 or 6 respectively was passed through the disk. The sample solution also contained 0.5 mg.L<sup>-1</sup> of Mn(II) and Na-DDTC (0.1% w/v). The flow-rate was 40-60 ml.min<sup>-1</sup>. After the extraction, the disk was dried completely by passing air through it. The extracted chromium species was desorbed from the disk by 5 ml of acidified methanol at a flow rate of 5-10 ml.min<sup>-1</sup>.

The eluting solution was collected in a 23 × 200 mm test tube which was placed under the stem of the extraction funnel. The chromium contents were then determined by AAS using an external calibration curve.

## ANALYSIS OF WATER SAMPLES

### Determination of Cr(VI)

Cr(VI) content of the samples was determined by adjusting the pH of the solution to 1.5 and maintaining the Mn(II) concentration at 0.5 mg.L<sup>-1</sup> and preconcentration and elution procedure was followed as described above.



**Figure 2.** Effect of pH on the recovery percentage of  $50 \mu\text{g.l}^{-1}$  of each of Cr(VI) and Cr(III).

**Table 2.** Optimized conditions for determination of Cr(VI /III).

Parameter	Chromium(VI)	Chromium(III)
pH	1-2	4-9
DDTC concentration (w/v %)	0.01-1	0.05-1.0
Eluent flow-rate ( $\text{ml.min}^{-1}$ )	4.0	4.0

#### Determination of Cr(III)

Cr(III) content of the samples was determined after adjusting the pH to 6 and maintaining the Mn(II) concentration at  $0.5 \text{ mg.L}^{-1}$ , and preconcentration and elution was performed as described above.

#### Analysis of ground water samples

The ground water samples were first passed through a  $45 \mu\text{m}$  (Millipore) Nylon filters to remove suspended particles. The Cr(VI) and Cr(III) contents of ground water samples were analyzed by adjusting pH to 1.5 and 6 by addition of  $0.5 \text{ mg.L}^{-1}$  of Mn(II), respectively and subjecting it to preconcentration and elution as described above.

## RESULTS AND DISCUSSION

Selection of optimum conditions for extraction of Cr(VI)

#### Effect of pH

It was observed that, DDTC complex of Cr(VI) is efficiently retained on a multiwalled carbon nanotube membrane disk in the 1-2 pH range. However, according to Figure 2, there is significant decrease in retention efficiency at pH=3 and no sorption of Cr(VI) was noticed

in the 4-8 pH range, but was observed that, DDTC complex of Cr(III) is efficiently retained on a multiwalled carbon nanotubes membrane disk in the 4-8 pH range. Hence, the pH of the sample solutions was adjusted to 1.5 by addition of dilute HCl throughout the experiments.

#### Optimization of Na-DDTC concentration

In order to investigate the influence of the Na-DDTC concentration on the quantitative extraction of chromium, the concentration of the ligand in 50 ml portions of sample solutions each containing  $10 \mu\text{g}$  of Cr(VI) was maintained (0.01% to 1% w/v). In all cases, the extraction of Cr(VI) was found to be quantitative (Table 2). Hence, subsequent SPE experiments were carried out with 0.1%w/v of the ligand.

#### Effect of different eluents

In order to select the most effective eluent for the quantitative extraction of the sorbed chromium species, after the extraction of  $25 \mu\text{g}$  of chromium from 50 ml of water, the retained chromium species were stripped with various amounts of different solvents. The results are

**Table 3.** Effect of different eluting solvents on Percentage recovery of chromium adsorbed on the disk <sup>a</sup>.

Stripping solution	% Recovery					
	2 ml		5 ml		10 ml	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Methanol	39.2(3.5) <sup>b</sup>	5.8(2.9)	79.3 (2.4)	86.3(1.5)	100.0(1.2)	99.6(2.4)
Acidified methanol <sup>c</sup>	46.1(1.6)	60.9(3.5)	60.2(1.4)	74.9(2.8)	98.9(1.8)	99.5(2.3)
Ammoniacal methanol <sup>d</sup>	27.2(2.6)	41.9(3.5)	30.2(3.3)	50.8(1.7)	82.4(2.2)	95.4(3.6)
Ethanol	46.5(1.5)	47.0(3.0)	50.5(3.5)	50.9(2.5)	90.5(3.1)	95.5(2.6)
1-Propanol	37.5(2.2)	28.0(3.0)	40.4(2.5)	47.9(1.5)	75.6(2.5)	82.0(1.5)
Formic acid(1M)	28.0(2.2)	21.8(2.0)	38.2(3.0)	35.1(1.7)	77.2(3.5)	80.5(2.2)
Hydrochloric acid(3M)	37.4(2.2)	34.8(1.7)	37.5(2.9)	59.2(1.9)	65.5(1.5)	78.2(1.5)
Hydrochloric acid(1M)	27.5(3.0)	35.8(2.1)	37.2(1.8)	46.5(2.8)	53.7(2.1)	59.3(2.8)
Nitric acid(3M)	36.6(1.0)	40.7(2.9)	38.2(1.2)	48.7(3.0)	57.6(3.0)	68.2(0.5)
Nitric acid(1M)	47.2(2.8)	45.8(1.5)	78.5(2.4)	68.2(1.8)	77.1(3.0)	83.2(0.7)

<sup>a</sup> Initial samples contained 25 µg of each Cr(III) and Cr(VI) in 50 ml water, <sup>b</sup> Values in parentheses are RSDs based on five individual replicate analysis, <sup>c</sup> Acidified solvents obtained by addition of 0.01M HCl, <sup>d</sup> Ammoniacal solvents obtained by addition of 0.1M NH<sub>3</sub>.

tabulated in Table 3. It is noteworthy that in all cases the concentrations of Mn(II) and Na-DDTC were 0.5 mg.L<sup>-1</sup> and 0.1% w/v, respectively. Our experiments revealed that 10 ml of methanol acidified with 0.01M HCl is able to remove the retained chromium (VI) quantitatively.

### Selection of optimum conditions for extraction of Cr(III)

#### Effect of pH

The influence of the pH of aqueous samples for the recovery of 10 µg of Cr(III) from 50 ml of solution was studied in the pH range of 2.0-8.0. The pH was adjusted using 0.1 M of either hydrochloric acid or sodium hydroxide solutions. The results shown in Figure 2, indicated that Cr(III) ion can be retained quantitatively by the multiwalled carbon nanotube membrane disk at pH =6. Higher pH values (>9) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks (Nayebi and Moghimi, 2006).

#### Effect of Na-DDTC concentration

The Na-DDTC concentration was varied from 0.01-1%w/v during the sorption of Cr(III)-DDTC complex on multiwalled carbon nanotubes membrane disk in the presence of manganese(II). Extraction of 20 µg Cr(III) from 50 ml aqueous solutions under the optimal experimental conditions was conducted by varying the amount of ligand from 0.01%w/v to 1.00%w/v. In all cases, the extraction of Cr(III) was found to be quantitative. The results are accorded in Table 2.

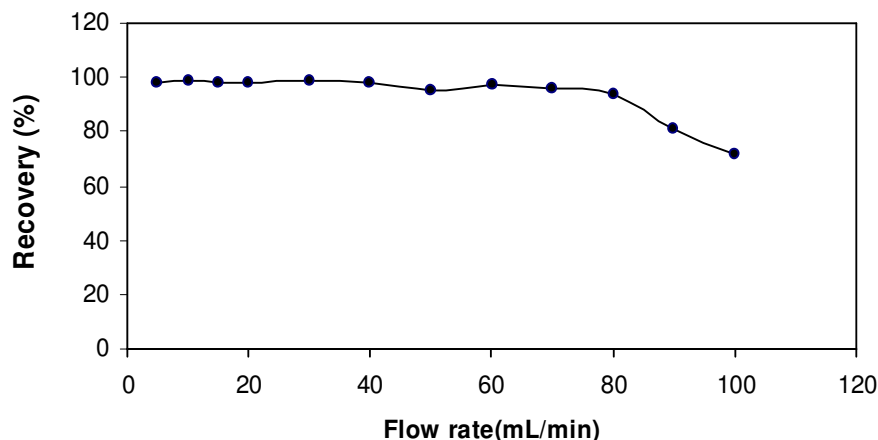
Therefore, concentration of Na-DDTC was maintained at 0.1%w/v throughout the experiments.

#### Effect of Mn(II)

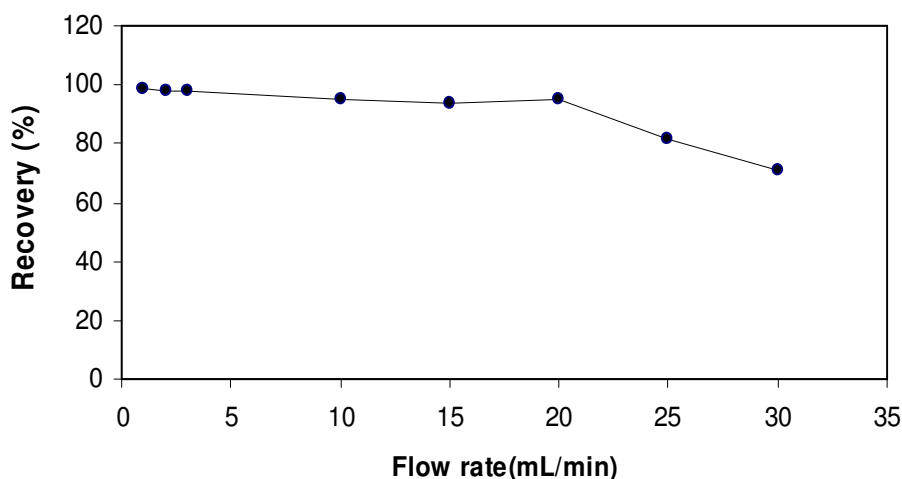
Presence of 1-2 mg.L<sup>-1</sup> of Mn(II) in the sample solution results a ten-fold enhancement of the flame AAS signal due to increased retention efficiency of Cr(III). Addition of 10 mg.L<sup>-1</sup> of Zn(II), Fe(II) and Fe(III) instead of Mn(II) resulted in two – three and five – fold enhancement of flame AAS signal of Cr(III) respectively. However, in the presence of 5 mg.L<sup>-1</sup> of Mn(II) in the sample, the addition of 10 mg.L<sup>-1</sup> of Zn(II), Fe(II) and Fe(III) have no influence. Therefore, an overall concentration of 5 mg.L<sup>-1</sup> of Mn(II) in the sample solution was selected in subsequent experiments. There is Cr(VI) in form of anionic, but Cr(III) is cationic therefore the addition 1-2 mg.L<sup>-1</sup> of Mn(II) to sample solution was found to provide maximum signal for Cr(III) during its sorption on C18 bonded silica gel in the presence of DDTC as the chelating agent. It was also noted that the addition of 1-2 mg.L<sup>-1</sup> of Mn(II) results in ten-fold enhancement in the flame AAS signal due to increased retention efficiency of Cr(III).

#### Effect of eluent acidity

Cr(VI) and Cr(III) complexes are eluted quantitatively only with acidified methanol (> 0.1 M in HCl or HNO<sub>3</sub>). Hence, acidified methanol (0.1 M HCl in methanol) was used to strip the chromium species sorbed on multiwalled carbon nanotubes membrane disk in the presence of Mn (II) – DDTC chelate (Table 3).



**Figure 3.** Effect of flow rates of the sample solutions on the recovery percentage of  $50 \mu\text{g.L}^{-1}$  of each of Cr(VI) and Cr(III).



**Figure 4.** Effect of flow rates of the stripping solutions using 5 ml methanol on the recovery percentage of  $50 \mu\text{g.L}^{-1}$  of each of Cr(VI) and Cr(III).

### Effect of flow rates

The effect of flow rates of the sample solutions on the retention and recovery of Cr(III) and Cr(VI) were investigated. It was found that in the range of 8-80  $\text{ml.min}^{-1}$ , the retention of Cr(III) and Cr(VI) by the multiwalled carbon nanotubes membrane disk, is hardly affected by the sample solution flow rate. Similar results for the extraction of inorganic and organic materials by multiwalled carbon nanotubes octadecyl silica membranes disks have already been reported (Nayebi and Moghimi, 2006) (Figure 3). The effect of flow rates of the stripping sample solutions on the retention and recovery of Cr(III) and Cr(VI) were investigated. On the other hand, quantitative stripping of Cr(III), Cr(VI) ions

from the disk was achieved at a flow rate range of 1-20  $\text{ml.min}^{-1}$ , using 5 ml of methanol (Figure 4).

### Interfering ions

The interferences due to coexisting ions on the determination of  $0.5 \mu\text{g.ml}^{-1}$  of Cr(VI) or Cr(III) were investigated under the optimum experimental conditions. It was concluded that  $\text{Na}^+$  ( $50000 \text{ mg.L}^{-1}$ ),  $\text{K}^+$  ( $1000 \text{ mg.L}^{-1}$ ),  $\text{Mg}^{2+}$  ( $2500 \text{ mg.L}^{-1}$ ),  $\text{Ca}^{2+}$  ( $1000 \text{ mg.L}^{-1}$ ),  $\text{Fe}^{2+}$  ( $1000 \mu\text{g.L}^{-1}$ ),  $\text{Fe}^{3+}$  ( $5000 \mu\text{g.L}^{-1}$ ),  $\text{Cd}^{2+}$  ( $1000 \mu\text{g.L}^{-1}$ ),  $\text{Pb}^{2+}$  ( $5000 \mu\text{g.L}^{-1}$ ),  $\text{Cu}^{2+}$  ( $5000 \mu\text{g.L}^{-1}$ ),  $\text{Ni}^{2+}$  ( $1000 \mu\text{g.L}^{-1}$ ),  $\text{Mn}^{2+}$  ( $5000 \mu\text{g.L}^{-1}$ ) and  $\text{Zn}^{2+}$  ( $10000 \mu\text{g.L}^{-1}$ ) do not interfere in determination of chromium (Table 4).

**Table 4.** Percent recovery of Cr(III) and Cr(VI) from binary mixtures <sup>a</sup> and percent recovery of Cr(III) and Cr(VI) from the multiwalled carbon nanotubes membrane disk in the presence of 0.02 M of different counter ions <sup>b</sup>.

Foreign ion	Amount taken	% Recovery of Cr(III)	% Recovery of Cr(VI)
Na <sup>+</sup>	2500 mg <sup>a</sup>	99.2(3.5) <sup>c</sup>	99.0(2.7)
K <sup>+</sup>	50 mg	99.2(1.9)	99.0(1.9)
Mg <sup>2+</sup>	125 mg	98.7(1.5)	98.8(2.8)
Ca <sup>2+</sup>	50 mg	100.1(1.6)	99.7(3.0)
Fe <sup>2+</sup>	0.050 mg	98.4(1.9)	98.7(1.6)
Fe <sup>3+</sup>	0.250 mg	99.8(2.9)	99.0(2.0)
Cd <sup>2+</sup>	0.050 mg	99.7(1.2)	99.0 (2.5)
Pb <sup>2+</sup>	0.250 mg	99.8(2.6)	94.7(2.1)
Cu <sup>2+</sup>	0.250 mg	99.2(3.0)	99.2(2.8)
Ni <sup>2+</sup>	0.050 mg	99.2(2.1)	99.0 (2.7)
Mn <sup>2+</sup>	0.250 mg	99.0(2.2)	95.4(2.7)
Zn <sup>2+</sup>	0.500 mg	99.4(1.7)	99.3(2.8)
Nitrite	0.02 M <sup>b</sup>	99.7(3.5)	99.3(2.2)
Nitrate	0.02 M	98.2(1.0)	98.8(1.9)
Acetate	0.02 M	99.7(1.5)	99.5(2.8)
Picrate	0.02 M	99.1(3.6)	99.0(3.0)
Chloride	0.02 M	99.4(1.9)	99.7(1.6)
Dihydrogen phosphate	0.02 M	99.2(2.9)	98.7(3.0)
Perchlorate	0.02 M	98.7(3.0)	99.1(2.5)
Iodate	0.02 M	98.8(2.6)	99.1(3.1)
Vanadate	0.02 M	98.9(3.0)	99.2(2.8)

<sup>a</sup> Initial samples contained 25 µg of each Cr(III) and Cr(VI) in 50 ml water. <sup>b</sup> Initial samples contained 25 µg of each Cr(III) and Cr(VI) and 0.02 M of each counter ion in 50 ml, <sup>c</sup> Values in parentheses are RSDs based on five individual replicate analysis.

**Table 5.** Analysis of synthetic mixtures of Cr(VI) and Cr(III).

Sample	Chromium taken (µg.L <sup>-1</sup> )		Chromium found (µg.L <sup>-1</sup> )	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	500(1.9) <sup>a</sup>	0.10(1.9)	495(2.2)	0.092(2.9)
2	0.1(1.2)	100(1.0)	0.093(1.1)	99.7(2.0)
3	500(2.0)	0.5(2.0)	480(2.6)	0.47(2.0)
4	0.5(1.9)	100(1.8)	0.49(2.0)	98.7(1.6)
5	0.5(1.3)	50.0(1.7)	0.49(1.6)	49.6(1.7)
6	50(2.7)	0.5(2.1)	49.3(2.7)	0.46(2.0)

<sup>a</sup> Values in parentheses are RSDs based on five individual replicate analysis.

Additionally, the counter anions influence on the extraction and subsequent clean-up and recovery of chromium species has been summarized in Table 4.

#### Effect of presence of Cr(VI) on determination of Cr(III) and vice versa

The influence of varying amounts of Cr(III) in Cr(VI) determination and of Cr(VI) in Cr(III) determination have been investigated and the results are accorded in Table

5. According to the results, 5000 and 1000 fold amounts of Cr(III) and Cr(VI) do not interfere in the determination of as low as 0.5 µg.L<sup>-1</sup> of Cr(VI) and Cr(III), respectively.

#### Analytical performance

Different volumes (10 ml – 2.5 L) of sample solutions containing 10 µg of each Cr(III) and Cr(VI) were passed through the disks. Under the best conditions, the chromium contents quantitatively were retained in all

**Table 6.** Recovery of chromium added to 1000 ml of different water samples (containing 0.1 M acetate at pH= 6.0) for Cr(III) and HCl at pH=1.5 for Cr(VI).

Sample	Cr(III) added ( $\mu\text{g}$ )	Cr(III)determined ( $\text{ng.ml}^{-1}$ )	Cr(VI) added ( $\mu\text{g}$ )	Cr(VI) determined ( $\text{ng.ml}^{-1}$ )
Tap water Tehran	0.0	2.72 (1.1) <sup>a</sup>	0.0	0.14 (0.9) <sup>a</sup>
	10.0	13.01 (1.3)	10.0	10.17 (1.2)
Snow water Tehran	0.0	2.01 (0.5)	0.0	0.09 (2.2)
	1.0	12.79 (2.1)	10.0	10.12 (0.5)
Ground water Varamin	0.0	70.91 (2.7)	0.0	0.81 (3.1)
	10.0	81.13 (2.3)	10.0	11.02 (1.3)
Rain water Tehran	0.0	2.03 (1.6)	0.0	0.10 (1.4)
	10.0	12.98 (1.8)	10.0	10.13(1.7)

<sup>a</sup> Values in parenthesis are RSDs based on three individual replicate analyses.

cases. Hence, by considering the final elution volume of 10 ml and the break through volume of about 2.5 L, an enrichment factor of about 250 is easily achievable. The maximum capacity of the disks were determined by passing 50 ml portion of sample solution containing 800  $\mu\text{g}$  of Cr(III) and 0.1 M acetate buffer at (pH=6), and 0.1%w/v Na- DDTC, also by passing 50 ml portion of sample solution containing 800  $\mu\text{g}$  of Cr(VI) and HCl at pH=1.5 and 0.1%w/v Na-DDTC, followed by the determination of the retained metal ions in the eluting solution using FAAS and an external calibration graph. The maximal capacity of the disk obtained from three individual replicate measurements was 498 3  $\mu\text{g}$  Cr(III) and 487 2  $\mu\text{g}$  Cr(VI) on the disk, respectively.

### Analysis of real samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Cr(III) and Cr(VI) from different water samples. Tap water (5 min after operation, Tehran (20th December 2012), ground water (Varamin-Charm Shahre, 7 January 2012), snow water (Tehran, 4 January 2012), rain water (Tehran, 10 December 2013). The samples were analyzed and the results are listed in Table 6.

The amounts of Cr(III) were found to be in the range of 2.01-71.13  $\mu\text{g.L}^{-1}$  and Cr(VI) 0.09-1.02  $\mu\text{g.L}^{-1}$ . Cr(VI) is detected in water samples which have been preserved for less than 4 min in 0.01 M HCl (Table 6). Real samples marked 1 to 5, were collected at the at the distances of 5, 100, 250, 350 and 500 m of the total waste water of electroplating plants in the eastern parts of Karaj, respectively. The total results obtained by the recommended procedure and ICP-AES have compared in Table 7. As it is seen, the results obtained by the

proposed method and ICP-AES are in agreement with each other.

Moreover, as it is expected, the chromium concentration decreases as the distance from the electroplating plants increases.

### Determination of methods detection limit

The limit of detection (LOD) of metal ions by this method was studied under optimal experimental conditions, calculated as  $\text{CLOD} = \text{Kb.Sb}/m$  (Nayebi and Moghimini, 2006) where Kb is a numerical factor of 3, Sb is the standard deviation of ten replicates blank measurements and m is the slop of calibration curve. The LOD obtained for Cr(III) and Cr(VI) were 21 and 12  $\text{ng.L}^{-1}$ , respectively. It is also noteworthy that detection limit for each preconcentrated sample should be divided to its enrichment factor.

### Calibration curve

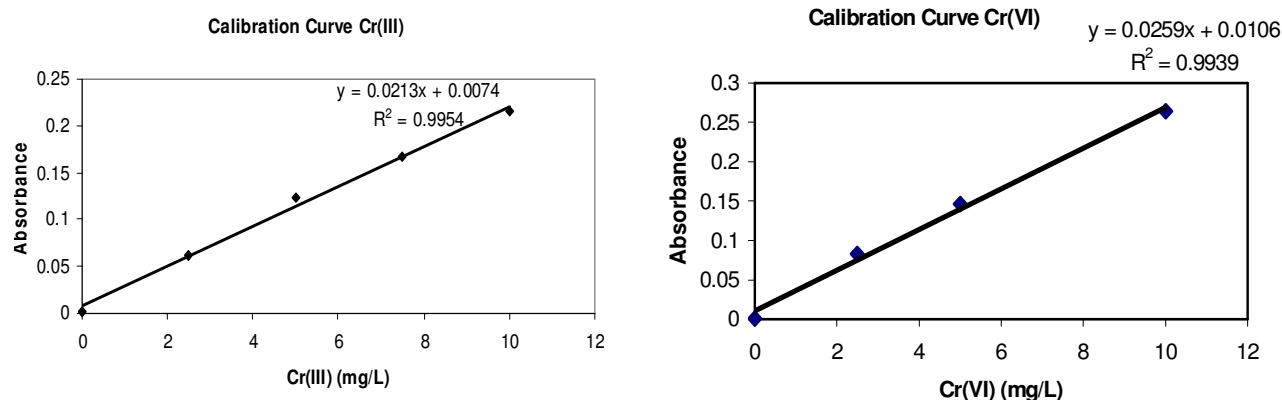
The standard stock solutions of Cr(III) and Cr(VI) (1000 ppm) were prepared by dissolving 0.4867 g of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (95%) and 0.2825 g of  $\text{K}_2\text{Cr}_2\text{O}_7$  (99.9%) in deionized water in 100 ml volumetric flasks respectively. Standard solutions of chromium were obtained by appropriate stepwise dilution of standard stock solutions. The calibration curve of Cr(III) and Cr(VI) solutions is represented in Figure 5 and the related regression is  $Y=0.0213X+0.0074$  and  $Y=0.0259X+0.0106$ , providing a correlation coefficient of  $R=0.9954$  and  $R=0.9939$ , respectively.



**Table 7.** Comparison of the total results of the proposed method with ICP-AES<sup>a</sup>.

Sample	Total chromium (mg.ml <sup>-1</sup> ) SPE-FAAS	Total chromium (mg.ml <sup>-1</sup> ) ICP-AES	F-test <sup>c</sup>	T-test <sup>d</sup>
1	16.5±0.5 <sup>b</sup>	16.6±0.7	3.1	0.5
2	14.6±0.3	14.7±0.5	1.8	0.8
3	7.9±0.8	8.1±0.7	2.7	0.9
4	3.6±1.3	3.5±1.1	2.0	0.6
5	1.8±0.9	1.7±0.9	2.1	0.7

<sup>a</sup>All real samples were diluted 50 times before analysis, <sup>b</sup> Mean ± standard deviations based on five individual replicate analyses, <sup>c</sup> Tabulated F-value for (4,4) degrees of freedom at p (0.95) is 6.39, <sup>d</sup> Tabulated T-value for 8 degrees of freedom at p (0.95) is 2.306.

**Figure 5.** Calibration curve of Cr(III) and Cr(VI) measured by SPE-AAS.**Table 8.** Comparison of published results of several on-line or several methods for determination of Cr(III) and Cr(VI).

Cr species	Technique	Sorbent	RSD (%)	LOD (µg/L)	Ref
Cr(VI) and Cr(III)	RP-HPLC	APDC	5	1.0	43
Cr(VI) and Cr(III)	SPE and AAS	CTAB and C <sub>18</sub> bonded silica disk	-	15, 20	19
Cr(VI)	TLC-UV	Titanic silicate	1.55	-	40
Cr(VI) and Cr(III)	Several methods	DDTC and C <sub>18</sub> bonded silica disk	2	0.03, 0.04	50
Cr(VI) and Cr(III)	Several methods	DDTC and Multiwalled carbon nanotubes (MWNTs) on C <sub>18</sub> bonded silica disk	1.7	0.01, 0.02	Present method

## Conclusion

The proposed solid phase extraction procedure based on octadecyl silica membrane disks modified with (SPFMWNTs) sub-unit is simple, highly sensitive, selective, reproducible and rapid, when compared with the previously reported SPE methods (Brunner et al., 2003; Choi and Choi, 2003; Zelder et al., 2005; Boll et al., 2005; Saber et al., 2005). The proposed SPE method possesses advantages such as easiness, and considerable selectivity in comparison with the previously reported procedures for isolation and determination of

chromium contents (Table 8). The maximum time taken for separation, preconcentration and monitoring of chromium species in 50 ml portions of water samples is at the most 10 min.

In the suggested procedure, any risk of analyte loss and or shift in equilibrium between the species has been minimized. The reproducibility of the procedure is near 2%. The proper preconcentration factor improves the LOD of the method by a factor of about 250. This procedure has the advantage of preconcentration of Cr(III) or Cr(VI) depending on the pH of the sample solution.

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