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PRECONCENTRATION AND DETERMINATION OF CHROMIUM SPECIES USING OCTADECYL SILICA MEMBRANE DISKS AND FLAME ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

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 396 ± 3 µg and 376 ± 2 µg for Cr(III) and Cr(VI), respectively. The detection limit of the proposed method is 49 and 43 $ng.L^{-1}$ for Cr(III) and Cr(VI), respectively. The proposed method was successfully applied for determination of Cr(III) and Cr(VI) in different water samples.

Keywords: Solid phase extraction, Sodium diethyldithiocarbamate, Flame atomic absorption spectrometry, Octadecyl silica membrane disk.

INTRODUCTION

Toxicological studies have proved that the degree of toxicity of an element directly depends on the species in which it is present. Cr(III) is considered as an essential micronutrient for humans and mammals in order to maintain glucose metabolism, where as Cr(VI) is a potentially carcinogenic agent[1]. The significant drawbacks of Cr(VI) are breathing disturbances, liver and digestion malfunctions, dermal corrosion and skin allergies[2]. Therefore, It is necessary to control the level of chromium in industrial effluent, natural and drinking waters. Speciation of chromium in environmental samples is of prime importance. Therefore there are numerous methods and techniques concerning chromium speciation and determination including liquid-liquid extraction after complex formation[3-4], solid-liquid extraction[5-8], LC-AAS[9-11], spectrophotometric[12], ICP-AES[13], and NAA[14]. However, some of these techniques are frequently expensive, time consuming and have elaborate sample preparation steps and low enrichment factors.

Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. SPE determinations can be carried out on different efficient ways. One of the most appropriative performation features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time[15-16]. The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed[17]. In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium[18-19] and lead[20]. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead[21-23], copper[24-26], silver[27-28], mercury[29-30], cadmium[31], palladium[32], Ce[33], and UO_2 [34].

The aim of this work was development of 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 octadecyl silica membrane disks. 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 grade (from Merck). Sodium diethyldithiocarbamate (Na-DDTC) (0.1%w/v) was prepared in deionized water. Organic eluents used were of HPLC grade. Standard solutions of Cr(III) and Cr(VI) were prepared by appropriate dilution of a 1000 $\mu g.mL^{-1}$ stock solutions made from chromium(III) chloride and Potassium dichromate, respectively.

Acidic buffer (pH=4,5) was prepared by mixing100,200g $CH_3COONa.2H_2O$ and150,30 mL HOAc glacial in 1L distilled water, respectively. The 0.45mm nitro-cellulose membrane filters used for the wastewater samples filtration, were obtained from Schleicher and Schuell, Germany (REFNO: 10404012) and 47 mm diameter solid phase extraction disks used for extraction and preconcentration of chromium from waste water samples, were supplied by Supelco ENVIDISK*TM* (Cat.NO.57171).

Apparatus

A Varian SpectrAA model 200 atomic-absorption spectrometer was used for determinations. The operational characteristics of employed parameters are summarized in Table 1.

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 ($L.min^{-1}$)	13.50
Acetylene flow rate ($L.min^{-1}$)	2.90

A Metrohm model 691 digital pH meter equipped with a combined glass-calomel electrode was used for pH adjustments and a Millipore filtration set has been employed, for solid phase extraction.

Proposed procedure

Extraction was performed with ENVI-DISKTM (47mm diameter and 0.5mm 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 was 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 reaches the surface of the disk. The disk should not be allowed to be dried. 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 air to contact the surface of the disk. 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 contains 0.5 $mg.L^{-1}$ of Mn(II) and Na-DDTC (0.1%w/v). The flow-rate was 40-60 $mL.min^{-1}$.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 $mL.min^{-1}$. The eluting solution was collected in a 23 mm×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 preconcentration and elution procedure was followed as described above.

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 $mg.L^{-1}$, and preconcentration and elution was performed as described above.

Analysis of ground water samples

The ground water samples were first passed through a 45 µm (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 $\mu g.mL^{-1}$ of Mn(II), respectively and subjecting 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, diethyldithiocarbamate complex of Cr(VI) is efficiently retained on a membrane disk in the 1-2 pH range. However, according to Fig.1, there is significant decrease in retention efficiency at pH=3 and no sorption of Cr(VI) was noticed 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 sodium diethyldithiocarbamate (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 µg of Cr(VI) was maintained(0.01%w/v 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.

Table - 2 : Optimized conditions for determination of Cr(VI /III)

Parameters	chromium(VI)	chromium(III)
pH	1-2	4-9
DDTC concentration (w/v %)	0.01-1	0.05-1.0
Eluent flow-rate ($mL.min^{-1}$)	4.0	4.0

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 20 µg of chromium from 50 mL of water, the retained chromium species were stripped with various amounts of different solvents. The results are tabulated in Table 3. It is noteworthy that in all cases the concentrations of Mn(II) and Na-DDTC were 0.5 $mg.L^{-1}$ 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.

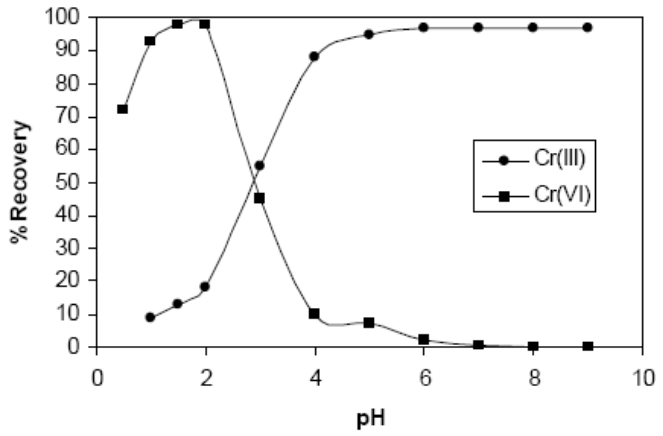

Fig. - 1: Effect of pH on the recovery percentage of 50 $\mu g.L^{-1}$ of each of Cr(VI) and Cr(III)

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 containing 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 Fig.1 indicate that Cr(III) ion can be retained quantitatively by the 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.[33]

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 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 0.05%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^{-1} 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) on the disk. Addition of 10 mg. L^{-1} 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^{-1} of Mn(II) in the sample, the addition of 10 mg.L^{-1} of Zn(II), Fe(II) and Fe(III) have no influence. Therefore, an overall concentration of 5 mg.L^{-1} of Mn(II) in the sample solution was selected in subsequent experiments.

Effect of eluent acidity

Cr(VI) and Cr(III) complexes are eluted quantitatively only with acidified methanol(> 0.1 *M* in HCl or HNO3). Hence, acidified methanol (0.1 *M* HCl in methanol) was used to strip the chromium species sorbed on membrane disk in the presence of Mn (II) –DDTC chelate (Table - 3).

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 mL.min^{-1}, the retention of Cr(III) and Cr(VI) by the membrane disk is hardly affected by the sample solution flow rate. Similar results for the extraction of inorganic and organic materials by octadecyl silica membranes disks have already been reported[34] (Fig. - 2).

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 form the disk was achieved at a flow rate range of 1-20 mL.min^{-1}, using 5 mL of methanol (Fig. - 3) .

Table - 3 : Effect of different eluting solvents on Percentage recovery of chromium adsorbed on the disk[a]

Stripping solution	% Recovery					
	2ml		5ml		10ml	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
Methanol	39.2(3.5) [b]	5.2(2.9)	71.3(2.4)	16.3(1.5)	100.0(0.8)	99.1(2.8)
Acidized methanol [c]	42.1(1.5)	60.2(3.5)	68.2(1.4)	74.3(2.8)	98.9(1.8)	99.5(2.7)
Ammoniacal methanol [d]	23.2(2.5)	41.2(3.5)	36.2(3.3)	50.7(1.7)	82.4(2.2)	95.3(3.6)
Ethanol	40.5(1.5)	47.6(3.0)	52.5(3.5)	50.2(2.5)	90.5(3.1)	95.2(2.6)
1-Propanol	32.5(2.1)	28.5(3.0)	41.4(2.5)	47.2(1.5)	75.6(2.5)	82.3(1.5)
Formic acid(1M)	22.0(2.3)	21.1(2.0)	35.2(3.0)	31.1(1.7)	77.2(3.5)	80.5(2.2)
Hydrochloric acid(3M)	31.4(2.1)	34.2(1.7)	36.5(2.9)	58.2(3.0)	65.5(1.5)	76.2(1.5)
Hydrochloric acid(1M)	20.5(3.2)	35.2(2.1)	36.2(1.8)	42.5(2.1)	53.7(2.1)	58.3(2.8)
Nitric acid(3M)	32.6(1.5)	40.1(2.9)	39.2(1.2)	47.7(3.2)	57.6(3.0)	69.2(0.5)
Nitric acid(1M)	40.2(2.5)	45.6(1.5)	75.5(2.4)	62.2(1.5)	77.1(3.0)	82.2(0.7)

[a] Initial samples contained 25 µg of each Cr(III) and Cr(VI) in 50 mL water
[b] Values in parentheses are RSDs based on five individual replicate analysis
[c] Acidified solvents obtained by addition of 0.1*M* HCl.
[d] Ammoniacal solvents obtained by addition of 0.1*M* NH_3

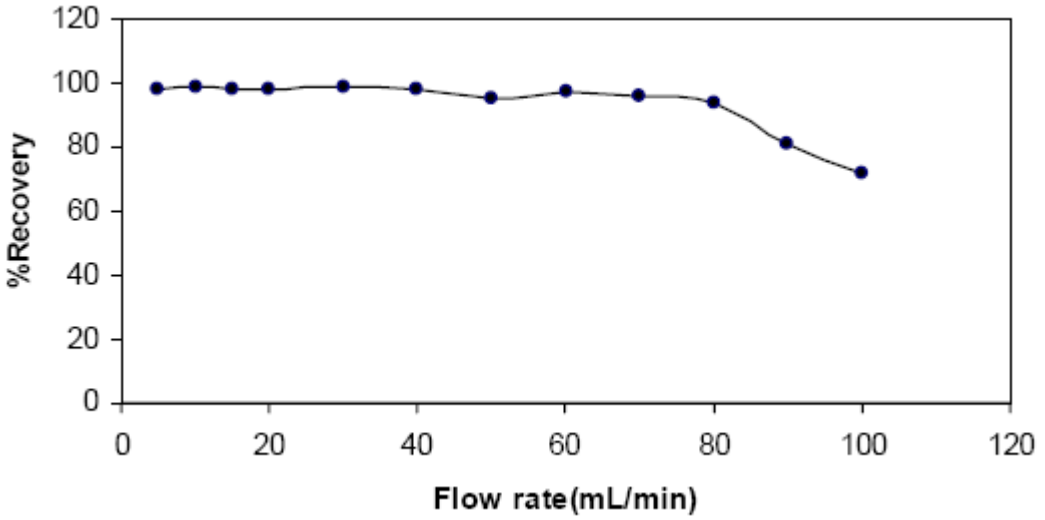

Fig. - 2 : Effect of flow rates of the sample solutions on the recovery percentage of 50 µg.L^{-1} of each of Cr(VI) and Cr(III)

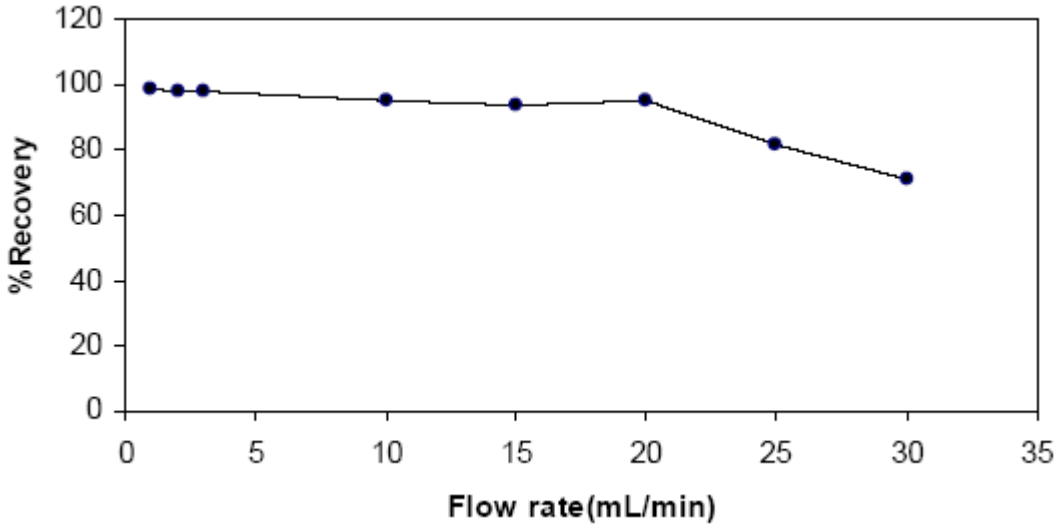

Fig. - 3 : Effect of flow rates of the striping solutions using 5 mL methanol on the recovery percentage of 50 µg.L^{-1} of each of Cr(VI) and Cr(III)

Interfering ions

The interferences due to coexisting ions on the determination of 0.5 µg.mL^{-1} of Cr(VI) or Cr(III) were investigated under the optimum experimental conditions. It was concluded that Na^{+} (50000 mg.L^{-1}), K^{+} (1000 mg.L^{-1}), Mg^{2+} (2500 mg.L^{-1}), Ca^{2+} (1000 mg.L^{-1}), Fe^{2+} (1000 µg.L^{-1}), Fe^{3+} (5000 µg.L^{-1}), Cd^{2+} (1000 µg.L^{-1}), Pb^{2+} (5000 µg.L^{-1}), Cu^{2+} (5000 µg.L^{-1}), Ni^{2+} (1000 µg.L^{-1}), Mn^{2+} (5000 µg.L^{-1}) and Zn^{2+} (10000 µg.L^{-1}) do not interfere in determination of chromium (Table - 4). Additionally, the counter anions influence on the extraction and subsequent clean-up and recovery of chromium species has been summarized in Table 5.

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 6.

Table 4 - Percent recovery of Cr(III) and Cr(VI) from the membrane disk in the presence of 0.02 *M* of different counter ions[a]

Counter ion	% Recovery of Cr(III)	% Recovery of Cr(VI)
Nitrite	99.7(3.5) [b]	99.9(2.7)
Nitrate	98.2(1.7)	98.8(1.9)
Acetate	99.7(2.5)	99.5(2.8)
Picrate	99.1(3.6)	99.0(3.0)
Chloride	99.4(1.9)	99.7(1.6)
Dihydrogen phosphate	99.2(2.9)	98.7(3.0)
Perchlorate	98.7(3.0)	99.1(2.5)
Iodate	98.8(2.6)	99.1(3.1)
Vanadate	98.9(3.0)	99.2(2.8)

[a] Initial samples contained 25 µg of each Cr(III) and Cr(VI) and 0.02 *M* of each counter ion in 50 mL.
[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table - 5 : Percent recovery of Cr(III) and Cr(VI) from binary mixtures[a]

Foreign ion	Amount taken (mg)	% Recovery of Cr(III)	% Recovery of Cr(VI)
Na^{+}	2500	99.2(3.5) [b]	99.9(2.7)
K^{+}	50	99.2(1.7)	99.8(1.9)
Mg^{2+}	125	98.7(2.5)	98.5(2.8)
Ca^{2+}	50	100.1(3.6)	99.7(3.0)
Fe^{2+}	0.050	98.4(1.9)	98.7(1.6)
Fe^{3+}	0.250	99.8(2.9)	99.7(3.0)
Cd^{2+}	0.050	99.7(3.0)	100.1(2.5)
Pb^{2+}	0.250	99.8(2.6)	99.7(3.1)
Cu^{2+}	0.250	100.2(3.0)	99.2(2.8)
Ni^{2+}	0.050	99.2(2.1)	100.1(2.7)
Mn^{2+}	0.250	99.0(2.2)	99.6(2.7)
Zn^{2+}	0.500	99.4(1.7)	99.3(2.8)

[a] Initial samples contained 25 µg of each Cr(III) and Cr(VI) in 50 mL water.
[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table - 6 : Analysis of synthetic mixtures of Cr(VI) and Cr(III)

Sample	Chromium taken ($\mu g.L^{-1}$)		Chromium found ($\mu g.L^{-1}$)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)
1	500(1.8) [a]	0.10(1.9)	495(2.0)	0.092(1.9)
2	0.1(1.2)	100(1.0)	0.093(1.1)	99.2(1.0)
3	500(2.0)	0.5(2.0)	480(2.6)	0.49(2.0)
4	0.5(1.9)	100(1.8)	0.49(2.0)	98.4(1.6)
5	0.5(1.3)	50.0(1.7)	0.49(1.6)	49.4(1.7)
6	50(2.7)	0.5(2.1)	49.3(2.7)	0.48(2.0)

[a] Values in parentheses are RSDs based on five individual replicate analysis.

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 1 " of Cr(VI) and Cr(III), respectively.

Analytical performance

Different volumes (10mL – 2.5L) of sample solutions containing10µg of each Cr(III) and Cr(VI) were passed through the disks. Under the best conditions, the chromium contents quantitatively were retained in all cases. Hence, by considering the final elution volume of 10 mL and the break through volume of about 2.5L, an enrichment factor of about 250 is easily achievable. The maximum capacity of the disks was determined by passing 50 mL portion of sample solution containing 800 µg 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 µg 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 396 ± 3 µg Cr(III) and 376 ± 2 µg 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 minutes after operation ,Tehran 20 December 2004), ground water (Varamin-Charm Shahre, 7 January 2004), snow water (Tehran , 4 January 2004), rain water (Tehran, 10 December 2003).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 µg.L^{-1} and Cr(VI) 0.09-1.02 µg.L^{-1}. Cr(VI) is detected in water samples which have been preserved for more than 4 hrs in 0.01 *M* HCl (Table - 7).

Table - 7 : 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 (µg)	Cr(III)determined (ng.mL^{-1})	Cr(VI) added (µg)	Cr(VI) determined (ng.mL^{-1})
Tap water [a]	0.0	2.72 (1.1) [a]	0.0	0.14 (0.9)
	10.0	13.01 (1.3)	10.0	10.17 (1.2)
Snow water	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	0.0	70.91 (2.7)	0.0	0.81 (3.1)
	10.0	81.13 (3.3)	10.0	11.02 (1.3)
Rain water	0.0	2.03 (0.6)	0.0	0.10 (0. 4)
	10.0	12.98 (0.8)	10.0	10.13(1.7)

[a] Values in parenthesis are RSDs based on three individual replicate analyses.

Determination of methods detection limit

To evaluate the detection limit of the proposed method, at first the standard deviations of blank solutions were determined under the optimized condition by using the equation (1). The equation (1) illustrates relation of statistic estimation for LOD of method where, "x min is the detection limit; Xs The equation (1) illustrates relation of statistic estimation for LOD of method where, "x min is the detection limit; Xs and Xb represent means values of sample and blank solution determinations, respectively. Numerical amount of tabulated t in related tables for confidence level of p(95%) and 4 degree of freedoms is 2.78 that the amount of N in equation (1) is number of replicates of sample or blank determination. By calculation of these values for determination of each sample (Table 8), detection limits of 49 ng.L^{-1} and 43 ng.L^{-1} for Cr(III) and Cr(VI) were obtained, respectively. It is also noteworthy that detection limit for each preconcentrated sample should be divided to its enrichment factor.

$$\Delta X_{\min} = \overline{X}_s - \overline{X}_b > t S_b \sqrt{\frac{N_s + N_b}{N_s . N_b}} \qquad (1)$$

Table - 8 : Blank determination used for calculation of LOD of the method

Blank solution	Cr(VI) (mg/L)	Cr(III) (mg/L)
1	1.03× 10-3	2.04 ×10-3
2	1.03 × 10-3	2.01× 10-3
3	2.02 × 10-3	9.98 × 10-4
4	2.01× 10-3	9.95 × 10-4
5	1.99× 10-3	1.01 × 10-3
	Sb =1.40 ×10-5	Sb =1.62× 10-5
	Xb=1.01× 10-3	Xb=2.01× 10-3

Calibration curve

The calibration curve of chromium solutions is represented in Fig. 4 and the related regression is Y=0.0056X-0.002 providing a correlation coefficient of R2=0.9994.

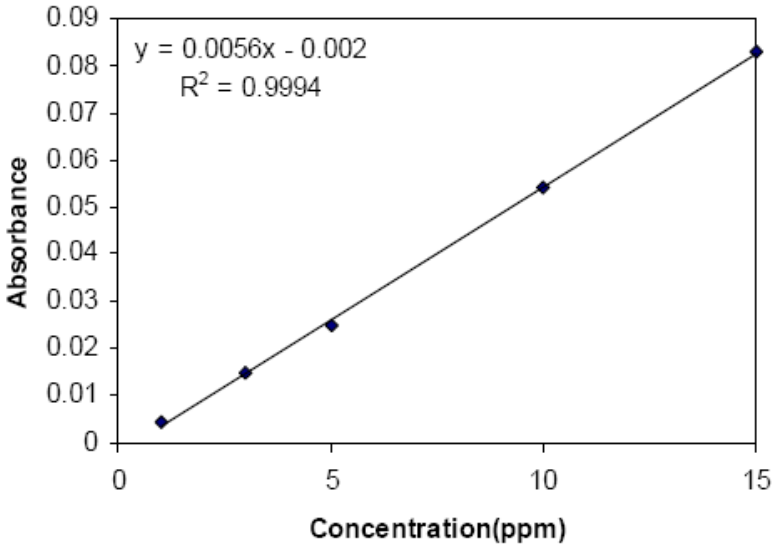

Fig. - 4 : Calibration curve of chromium measured by SPE-AAS

Table - 9 : 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 (III)	FIA - AAS	Lanthanum hydroxide	-	0.5	36
Cr (VI) and total chromium	FIA - AAS	1,5-Diphenylcarbazide	-	2	37
Cr (VI)	TLC - UV	Titanic silicate	1.55	-	38
Cr (VI) & Cr (III)	Several methods	DDTC and C_{18} bonded silica disk	2	0.03 Cr(VI) 0.04 Cr (III)	Present method

Conclusion

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 9). 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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