

Preconcentration, Determination and Speciation of Chromium(III) Using Solid Phase Extraction and Flame Atomic Absorption Spectrometry

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A novel, reliable and reproducible method for speciation and determination of the traces amounts of chromium(III) in the waste water has been developed. The method was based on complex formation on the surface of the ENVI-18 DSK™ disks followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution was efficient and quantitative. The effects of potential interfering ions, pH, ligand amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to be about 1500 mL providing a preconcentration factor of 300. The maximum capacity of the disks was found to be $225 \pm 3.9 \mu\text{g}$ for Cr^{3+} . A limit of detection of 0.02 ng.mL^{-1} was obtained, and the method was applied for determination of chromium in electroplating industries waste water located in the eastern regions of Tehran.

INTRODUCTION

Chromium speciation has a prime importance in different branches of natural sciences. The importance of chromium speciation originates from widespread participation of this element in various environmental and biological samples. Hence, new investigations have been oriented in this field. The major sources of entrance of chromium to the environment are steel, electroplating, tanning and chemical industries, oxidative dyeing, cooling water towers, corrosion inhibitors used in water pipes and containers and sanitary landfill leaching.

Chromium occurs essentially only in two stable oxidation states in nature which are Cr(III) (trivalent) and Cr(VI) (hexavalent). It has been proved that the traces amounts of Cr(III) are necessary for mammals health in order to maintain glucose, lipid and perform protein metabolism. However, Cr(VI) is known to have an extremely toxic effect on human organisms. This property is attributed to high oxidation potential and relatively small size of this ion. Accumulation and inhalation of hexavalent chromium bearing substances, lead to bronchitis, pneumonitis, asthma, nasal septum and inflammation of the larynx and liver and increased incidence of bronchogenic carcinoma. Meanwhile, direct contact with these materials may cause dermatitis, dermal necrosis, skin allergies and dermal corrosion.³⁻⁵

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Presence of chromium in different environmental and biological samples at very low levels necessitates its separation and introduction of a novel preconcentration step prior to determination.

A literature survey reveals that there are numerous techniques and procedures concerning determination of chromium contents in different matrices, including spectrophotometric,⁶ inductively coupled plasma atomic emission spectrometry (ICP-AES),⁷ neutron activation analysis (NAA),⁸ X-Ray absorption spectrometry,⁹ and spectrophotometric sequential injection system.¹⁰ The main restrictions of the latter techniques are expensive instrumentation, time consuming and elaborate sample preparation, high relative standard deviations (RSDs), inadequate enrichment factor and low sensitivity.

Coprecipitation and liquid-liquid extraction techniques as conventional methods have been employed for separation and enrichment of different metal species.^{11, 12} However, these methods are frequently time consuming, labor intensive and require to relatively large volumes of extra pure hazardous organic solvents. Additional concern is the disposal of the employed solvents which yields serious and considerable environmental problems. On the other hand, solid phase extraction (SPE) techniques are the best alternative for conventional classical methods due to selective removal of traces amounts of metal ions from their solutions with minimum use of toxic organic solvents. The most important adsorbents used in the SPE procedures are thiol cotton,¹³ green tea leaves,¹⁴ cellulose,¹⁵ silanized glass beads,¹⁶ polythioether foams,¹⁷ ion exchange or chelating resins,¹⁸ microcrystalline naphthalene,¹⁹ titanium dioxide (TiO₂),²⁰ and alumina.²¹ In the present work, we wish to introduce a unique and efficient SPE technique for determination and speciation of chromium(III) in the waste water of electroplating industries as the major constituent component of them.

We and other researchers have successfully modified the octadecyl membrane disks with some suitable ligands for selective separation and preconcentration of trace amounts of chromium,²² lead,²³⁻²⁵ mercury,²⁶ copper,²⁷⁻²⁸ silver²⁹⁻³⁰ cadmium,³¹ palladium,³² three valent cerium,³³ and uranyl (UO₂).³⁴

The recently synthesized and introduced ligand (Fig. 1.) (TEBD) is a three – dentate donating type (NNS), which is insoluble in water at neutral pH.

Our recent conductometric studies in acetonitrile revealed that the mentioned ligand can form a fairly stable and selective complex with Cr(III).³⁵ This observation encouraged us to test its capability as a suitable reagent for enrichment and separation of Cr(III) contents via solid phase extraction by using octadecyl bonded silica membrane disks. To the best of our knowledge, this is the first report on chemical speciation of chromium using TEBD.

EXPERIMENTAL

Reagents and materials

All chemicals were of analytical grade and used as received without any further purification. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt(II), and copper(II) and ultra pure organic solvents were of the highest purity and obtained from E.Merck, Darmstadt, Germany. Solid phase extractions were carried out by glassy membrane disks.

ENVI-18DSK™ 47mm diameter×0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70Å pore size) obtained from Supelco (Bellefonte, PA 16823). The employed disks were capable for separating bulky ion-pairs and neutral organic and organometallic molecules. The nylon filters (45 μm) used for filtration of water samples were purchased from S&S Company. Deionized water was prepared by the passing of double distilled water through Nano-pure ultrapure water system from Barnstead Company (U.S.A.) and was used throughout the experiments.

Apparatus

The NMR spectra were recorded on a Joel 90 MHz spectrometer, and TMS was used as internal reference. The FT-IR spectra were recorded on a Shimadzu 4300 instrument using KBr pellets. The MS spectra were recorded on a Shimadzu GC-14A gas chromatograph-mass spectrometer. Determination of chromium contents in working samples were carried out on a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow cathode lamp (HI-HCL) according to the recommendations of the manufacturers. These characteristics are tabulated in Table1.

Solid phase extractions were conducted by the mentioned membrane disks, in conjunction with a standard Millipore 47mm filtration apparatus equipped with a desktop vacuum pump. The pH measurements were carried out by an ATC pH meter equipped with a combined glass calomel electrode (EDT instruments, GP 353).

Sampling

Real samples of chromium were collected from eastern electroplating plants located in east of Tehran. The samples were collected from 1 m depth of the waste water containers. In Fig. 2, distribution of chromium content as a function of distance from electroplating industries in all seasons of 2004 has been demonstrated.

Synthesis of TEBD

The procedure for preparation of (E)-N¹-(1-thiophen-2-yl) ethylidene benzene-1, 2-diamine (TEBD) is as follows: A mixture of 1.26 g = 0.01 mol of 2-acetylthiophene, 1.08 g = 0.01 mol of 1, 2-phenylenediamine, and a small amount of *p*-toluene sulfonic acid (enough to catalyze the reaction) in 50 mL of benzene was refluxed for 7 hrs. The solvent was then evaporated and the residue was crystallized from 95% ethanol. The specifications of the yellow crystals obtained as product were: m.p.124-127°C; 1.9 g. yield 90%; IR (KBr) (ν_{max} /cm⁻¹): 3250 and 3195 (NH₂) 1608, 1470, 1312, 1225, 1018, 881, 765; MS. *m/z* (%): 216 (M⁺, 59). Anal. Calcd for C₁₂H₁₁N₂S (216.31): C, 66.43; H, 5.59; N, 9.5. Found: C, 66.7; H, 5.7; N, 8%. ¹H NMR (250.1 MHz, DCCl₃): δ 2.33 (3 H. s, CH₃), 3.72 (2 H. br., NH₂), 6.62 (1 H, d, *J* = 6.9 Hz, CH), 6.74-6.78 (2 H. m, 2 CH), 6.99 (1 H. t, *J* = 6.5 Hz, CH), 7.10 (1 H, dd, *J* = 3.5 Hz and *J* = 1.5 Hz, CH), 7.44-7.49 (2 H. m, 2 CH).

Sample extraction

The standard stock solutions of Cr(III) and Cr(VI) (1000ppm) were prepared by dissolving 0.4868g of CrCl₃.6H₂O (95%) and 0.2828 g of K₂Cr₂O₇ (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 external calibration graph for chromium obtained by flame atomic absorption spectrometry (FAAS) is shown in Fig. 3.

The performance steps of the employed solid phase extraction - flame atomic absorption spectrometry (SPE-FAAS) technique were as follows:

1) *Sample treatment*: The water samples were filtered through 45 μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol.L⁻¹ HNO₃ overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of chromium species. Then 5 mL of methanol was added to a 90 mL portion of each before analysis. The surface of the ENV1-18 DSKTM disks was not modified with TEBD and therefore could not retain Cr(III) ions properly. Instead, 10 mg of TEBD was dissolved in appropriate volume of an organic solvent (5 mL) miscible with water. The most suitable solvent under the experimental conditions was acetone. The TEBD solution was added to aqueous solution of chromium and the mixture was stirred gently.

2) *Disk cleaning and conditioning*: A disk was placed in the apparatus and was washed with 10 mL of methanol to remove all contaminants arising from manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. To insure optimal extraction of the analytes of interest, the disk was again washed with 10 mL of methanol, immediately followed by 10 mL of water, without letting the surface of the disk to be dried. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow-rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

3) *Sample addition*: After complete homogenization, accurate volumes of the sample solutions (100 mL portions) were transferred to the top reservoir of the disk apparatus. At the same time the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk is completely dried (about 5 minute).

4) *Analyte elution*: In order to elute the analyte selectively, exactly 5 mL of methanol was passed through the disk and collected into a 5.0 mL volumetric flask under the extraction funnel. It was found out that ultra pure alcoholic organic solvents were the best eluting agents. The concentrations of chromium species in the eluates were then determined by FAAS using external calibration graph.

RESULTS AND DISCUSSION

Evaluation the role of the ligand

Some preliminary experiments were performed for investigation of absence or presence of TEBD on the quantitative extraction of chromium species. It was concluded that the membrane disk itself does not show any tendency for the retention of chromium species, but introduction of 100 mL portions of aqueous chromium samples containing 10 μg of Cr(III) and 10 mg of TEBD leads to satisfactory retention of it (Table 2). The latter case is most probably attributed to the existence of a considerable interaction between chromium(III) species and the TEBD. It should be mentioned that formation of stable complexes between Cr(VI) and TEBD at pH=2 is probably due to ion pair formation mechanism. However, at pH higher than 2 the retention and percentage recovery of Cr(VI) species are negligible. Consequently, for separation and determination of Cr(VI),

it must be reduced to Cr(III) at the first step. Hence, before the extraction, 0.5 mL of sodium thiosulphate (0.1 mol.L^{-1}) must be added to the samples containing both species as a reducing agent. Therefore, the total chromium content was determined by following the above described method. Meanwhile, the Cr(VI) content was deduced by subtracting Cr(III) content from total chromium.

Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained chromium(III) species on the disks, 5 mL of various non organic (each containing 10 % V.V⁻¹ methanol) and different organic solvents were tested. The results are tabulated in Table 3. As it is seen, the best eluting solvents were found to be 5 mL of methanol or ethanol resulting quantitative elution of chromium species from the disk. It should be emphasized that presence of methanol in any kinds of employed solvents helps better contact of eluent with hydrophobic surface of the disk.

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2-7 by addition of hydrochloric acid or a suitable buffer such as sodium acetate - acetic acid or sodium dihydrogen phosphate - disodium hydrogen phosphate and then the solutions passed through the disks. Eventually, the metal ions were stripped by pure methanol or ethanol solutions followed by flame atomic absorption determination of the eluted chromium. Then, the percentage recovery at various pH values was determined (Fig. 4.) According to the results shown in Fig. 4 up to pH= 4, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is probably because the ion product in the sample solution becomes close to solubility product of chromium(III) hydroxide ($K_{sp}=1.6 \times 10^{-30}$) and subsequent precipitation of Cr(OH)_3 in the solution. Other solvents used for dissolving TEBD were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Fig. 4. Meanwhile, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame. Higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.³⁶

The influence of the flow-rate

One of the most important parameters affecting solid phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10-150 mL.min⁻¹, the retention of chromium species were not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Fig. 5.). Thus, the flow-rate was maintained at 65 mL.min⁻¹ throughout the experiment.

Quantity of the TEBD

The optimum amount of TEBD for the quantitative extraction of chromium(III) was also investigated by adding various amounts of it to the solution (between 2-15 mg). The results are listed in Table 4. The experimental results revealed that the extraction of

chromium(III) was quantitative using a sample solution containing more than 8 mg of TEBD. Hence, subsequent extractions were performed with 10 mg of TEBD.

Disks efficiency

Undoubtedly, one of the major parameters affecting in the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimal experimental conditions, it was found out that each ENVI-18DSK™ disk could perform at least 20 replicate analyses if organic eluting solvents are used. In the other hand, acidic eluents practically decrease the number of times a disk could be used to 14 replicates. These observations are represented in Fig. 6.

Analytical performance

Analysis of synthetic mixtures of Cr(III) and Cr(VI)

Synthetic mixtures of Cr(III) and Cr(VI) in different selected ratios were chosen and the recommended method was performed. The results have been demonstrated in Table 5. As it is obvious, the proposed method could be used for speciative determination of chromium species.

Diverse ions interferences

For selective separation and determination of Cr(III) ion from its binary mixtures containing diverse metal ions, an aliquot of aqueous solution (100 mL) involving 10 µg of each Cr(III) and Cr(VI) and microgram amounts of other cations were taken and the described method was followed. The results are tabulated in Table 6. As it is seen, the recoveries of the chromium ions in these cases were almost quantitative.

Break-through volume

The break-through volume of the sample solutions was determined by dissolving 10 µg of chromium(III) in 25, 50, 100, 250, 500, 1000 and 1500 mL of water and the proposed method was followed. In all cases, the extraction was found to be quantitative. Hence, the break-through volume for this procedure should be greater than 1500 mL. Consequently, by considering the final volume of 5 mL and the break-through volume of 1500 mL a preconcentration factor of 300 was easily achievable.

Disk capacity

The maximum capacity of the employed membrane disk was examined by introduction of 100 mL of an aqueous solution containing 800 µg of Cr(III) and 10 mg of TEBD. The stripped Cr(III) content was determined by FAAS. The maximum capacity of the disks was found to be 225 ± 3.9 µg of Cr(III) ion.

The detection limit

The detection limit (LOD) of the proposed method was determined under the optimal experimental conditions. The LOD estimated from $C_{LOD} = K_b S_b \cdot m^{-1}$ where S_b is the standard deviation of the blank measurements (5 replicates) and m is the slope of the

linear calibration curve.³⁷⁻³⁸ For a numerical factor of $K_b = 3$ and a preconcentration factor of 300, a detection limit of 0.02 ng.mL^{-1} was obtained.

The reproducibility of the present work for 5 individual replicate measurements yielded a RSD of 1.5 %.

Chromium speciation of the electroplating waste-water samples

In order to evaluate the applicability of the suggested method for real samples with different amounts of diverse ions, it was employed for the determination and speciation of chromium in the waste-water of electroplating industries located in eastern Tehran. The samples were collected at different distances from the industrial state. The results are listed in Table 7.

Real samples marked 1 to 6, were collected at the distances of 50, 100, 500, 1000, 2000 and 3000 meters of the total waste water channel of electroplating plants in spring of 2004, respectively. The total results obtained by the recommended procedure and ICP-AES have been compared in Table 8. As it is seen, the results obtained by the proposed method and ICP-AES are in agreement with each other. Moreover, as it was expected, the chromium concentration decreases as the distance from the electroplating plants increases.

Comparison of the efficiency of the proposed method with other techniques

The suggested procedure possesses advantages such as inexpensive instrumentations, low solvent consumption and disposal costs, reliable results, high sensitivity, and also allows high sample flow-rates up to 150 mL.min^{-1} over similar methods, therefore, is cheaper. It is also noteworthy that the recommended method does not need direct modification of the membrane disks. In Table 9, the efficiencies of different sorbents on monitoring chromium traces have been compared.

CONCLUSION

The recommended method is simple, cheap, facile, fast, selective, accurate and reproducible. The proclaimed major advantages of SPE disks include shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk, and decrease pressure drop which allows the sample processing at higher flow-rates; reduced channeling resulting from the use of smaller diameter sorbent and a greater mechanical stability of the sorbent bed.⁴⁶ The reproducibility of this method is at the most 2 %. The time required for extraction, stripping and analysis of chromium ion in 100 mL water samples is about 15 min. This procedure is applicable for separation and determination of Cr(III) in real samples.

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Key words: Chromium(III) Speciation, Solid Phase Extraction, Flame Atomic Absorption Spectrometry

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Fig. 1. Molecular structure of (E)-*N*¹-(1-thiophen-2-yl) ethylidene) benzene-1, 2-diamine (TEBD).

Fig. 2. Distribution template of chromium in all seasons of 2004 year.

Fig. 3. External calibration curve of chromium.

Fig. 4. Influence of sample pH and dissolving solvent of TEBD on the percentage recovery of chromium(III).

Fig. 5. The effect of the flow-rate on extraction percent of Cr(III).

Fig. 6. The influence of eluent type on disk efficiency.

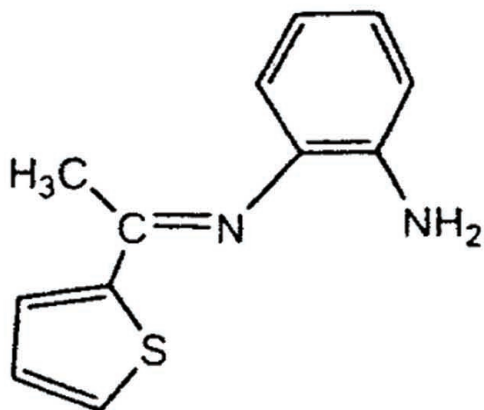


Fig. 1.

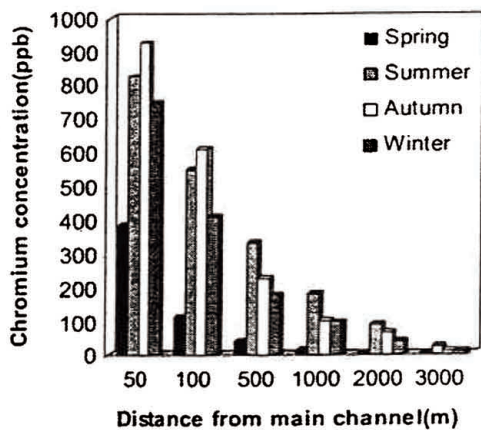


Fig. 2.

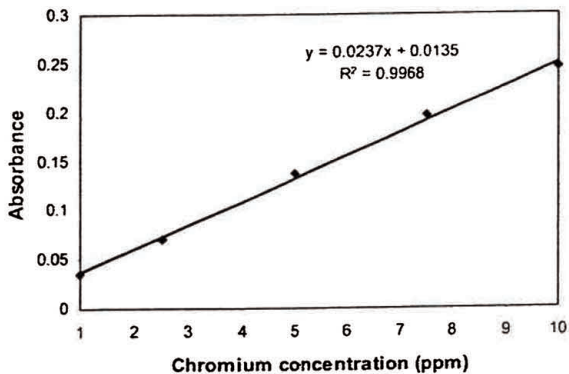


Fig. 3.

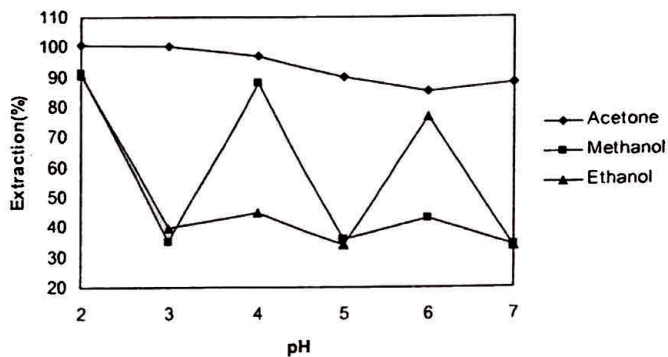


Fig. 4.

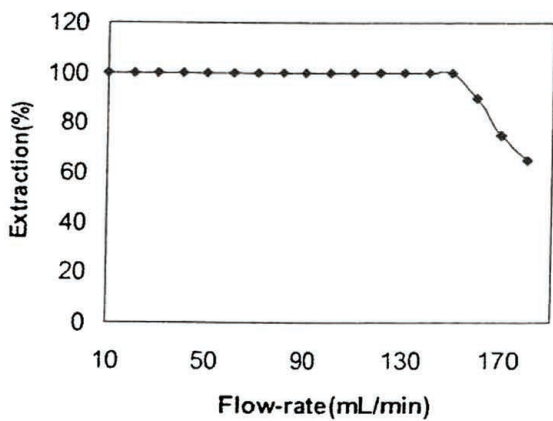


Fig. 5.

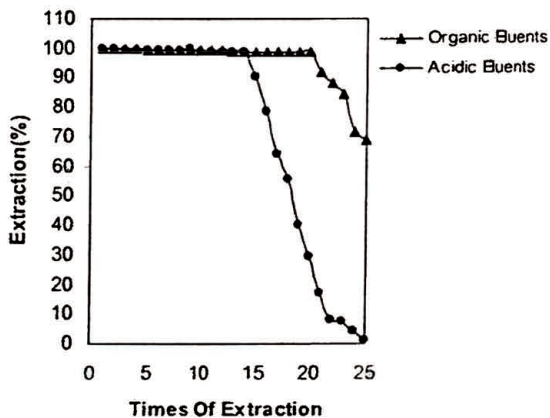


Fig. 6.

Table1. The operational conditions of the flame for determination of chromium

Slit width	0.2 nm
Operation current of H1-HCL	7.0 mA
Resonance fine	357.9 nm
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Length of air-acetylene burner	13/50 mm
Air flow	13/50 L.min ⁻¹
Acetylene flow	2.90 L.min ⁻¹

Table 2. The effect of presence of TEBD on extraction percent of Cr(III) ^a

TEBD	pH	Extraction percent of Cr(III)
Absence	2-7	0.00(6.3) ^b
Presence	2-7	100(0.4) to 88(1.2)

^a Initial samples contained 10 µg of Cr(III) in 100 mL of water.

^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 3. Recovery percent of chromium(III) species retained on membrane disks using 5 mL of different stripping solutions ^a

Stripping Solution	Recovery(%) of Cr(III)
HNO ₃ 3M (10 % V.V ⁻¹ methanol)	45 (3.3) ^b
HNO ₃ 1M (10 % V.V ⁻¹ methanol)	33 (1.5)
HBr 1M (10 % V.V ⁻¹ methanol)	30 (0.6)
HCl 1M (10 % V.V ⁻¹ methanol)	28.5 (0.6)
CH ₃ COOH 1M (10 % V.V ⁻¹ methanol)	40 (1.5)
2-Propanol	17 (4.2)
Methanol	100 (1.0)
Ethanol	99.5 (1.5)

^a Initial samples contained 10 µg of Cr(III) in 100 mL of water.

^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 4. Influence of the TEBD amount on the recovery of chromium(III) ions ^a

TEBD amount (mg)	Recovery(%) of Cr(III)
2	50 (0.4) ^b
4	64 (1.5)
5	80 (0.8)
8	95.8 (0.3)
10	100 (0.9)
15	100.1 (1.3)

^a Initial samples contained 10 µg of Cr(III) in 100 mL of water.

^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 5. Analysis of 100 mL of synthetic mixtures

Sample	Chromium taken (μg)		Chromium found (μg)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI) Cr(T)- Cr(III)
1	1.0	1.0	1.0(2.4) ^a	0.9(5.4)
2	10	10	10.2(3.1)	10.1(2.5)
2	100	100	99.9(1.4)	99.2(3.5)
4	1.0	100	0.96(0.8)	100.2(4.1)
5	100	1.0	99.5(5.2)	0.95(3.3)

^a Values in parentheses are RSDs based on five individual replicate analyses.

Table 6. Extraction of Cr(III) and Cr(VI) from mixtures containing interfering ions ^a

Foreign ion	Amount taken (μg)	Extraction(%) of Cr(III)	Extraction(%) of Cr(VI)
Li^-	3000	99.2 (1.2) ^b	99.1 (0.4)
Na^-	3000	99.8 (0.8)	99.7 (0.8)
K^-	3000	100.1 (0.4)	100 (0.9)
Mg^{2-}	2500	100.2 (0.3)	99.9 (0.6)
Ca^{2-}	3000	98.9 (0.9)	99.1 (0.3)
Sr^{2-}	2500	99.5 (0.5)	99.2 (1.2)
Ba^{2-}	2500	100.4 (0.5)	100 (1.1)
Zn^{2-}	250	99.8 (0.6)	100 (0.9)
Cd^{2-}	300	100 (0.8)	100.2 (0.9)
Pb^{2-}	200	100.2 (1.1)	101.4 (0.6)
Ni^{2-}	200	99.2 (0.9)	98.7 (0.8)
Co^{2-}	450	98.8 (1.1)	97.5 (1.2)
Cu^{2-}	500	99.4 (0.3)	99.3 (0.4)

^a Initial samples contained 10 μg of each Cr(III) and Cr(VI) in 100 mL of water.^b Values in parentheses are RSDs based on five individual replicate analyses.

Table 7. Determination of chromium in electroplating plants waste water

Sample	Cr(III) (ng.mL ⁻¹)	Cr(VI) (ng.mL ⁻¹)
1	102 ± 0.3 ^a	283 ± 0.2
2	42 ± 0.4	70 ± 0.6
3	19 ± 0.2	24 ± 0.3
4	8.0 ± 0.3	10 ± 0.6
5	4.0 ± 0.8	6.0 ± 0.7
6	1.50 ± 0.3	2.50 ± 0.2

^a Mean value ± standard deviations based on five individual replicate analyses.

Table 8. Comparison of the total results of the proposed method with ICP-AES ^a

Sample	Total chromium(ng.mL^{-1}) SPE-FAAS	Total chromium(ng.mL^{-1}) ICP-AES	F-test ^a	T-test ^b
1	385 ± 0.4 ^c	385.5 ± 0.6	2.2	1.5
2	112 ± 0.7	112.3 ± 0.4	3.1	0.8
3	43 ± 0.4	43.4 ± 0.5	1.6	1.4
4	18 ± 0.7	-	-	-
5	10 ± 1.1	-	-	-
6	4.0 ± 0.4	-	-	-

^a Tabulated F-value for (4, 4) degrees of freedom at p (0.95) is 6.39.

^b Tabulated T-value for 8 degrees of freedom at p (0.95) is 2.306.

^c Mean value \pm standard deviations based on five individual replicate analyses.

Table 9. Comparison of published methods for chromium determination by preconcentrative techniques

Technique	Employed sorbent	D.L. (ng.mL ⁻¹)		RSD(%)	Ref
		Cr(III)	Cr(VI)		
SIA-FAAS	activated alumina	81	42	<10	39
ICP-MS	modified polyacrylonitrile	0.06	0.06	<10	40
FAAS	PTFE packed column	-	0.8	3.2	41
TLC-UV	titanic silicate	-	-	1.55	42
ICP-AES	titanium dioxide	0.32	-	2.4	43
SPME-GC-FPD	poly amide coated fiber	2	-	7	44
FIA-FAAS	Zr(IV) & Zr(IV) phosphate	1.9	2.3	<3	45
SPE-FAAS	C ₁₈ octadecyl silica disks	0.02	-	<2	proposed method