Solid phase extraction of Cr(III) on micro crystalline modified with organic-solution-processable functionalized- nano graphene

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Abstract

A novel and selective method for the fast determination of trace amounts of Cr (III)ions in water samples has been developed. method has been developed for preconcentration of Cr on organic-solution-processable functionalized-graphene (SPFGraphene) adsorben in the pH range 5.0–10.0, prior to its spectrophotometric determination, based on the oxidation of bromopyrogallol red at $\lambda = 517$ nm. This method makes it possible to quantitize Cr in the range of 4.2×10^{-9} to 2.3×10^{-5} M, with a detection limit (S/N = 3) of 1.42×10^{-9} M. This procedure has been successfully applied to determine the ultra-trace levels of Cr in the environmental samples, free from the interference of some diverse ions. The precision, expressed as relative standard deviation of three measurements is better than 3.0%.

1. 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, whereas Cr(VI) is a potentially carcinogenic agent[1].Cr(III) at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [2-5].This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Cr(III) can bind to the cell membrane and hinder the transport process through the cell wall. Cr(III) at nearly 40ng mL-1 is required for normal metabolism of many living organisms[6]. On the other hand, Cr(III) is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Cr(III) is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) [7]. as well as spectrometric methods [10] .

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. Solid phase extraction 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[8-11].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[13]. In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium [14] and lead [11]. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead[15], copper [16], silver[19], mercury [17,19], cadmium [20], palladium [21], Ce[22] and UO_2 [12].

The used ligand is new and fairly selective and will not interfere in the determination process of Cr(III). Absorption spectrophotometry method (after preconcentration) was applied for determination of Cr based on the oxidation of bromopyrogallol red at 517 nm. Various effective parameters have been evaluated, and the developed procedure has been successfully employed for the quantitation of ultra-trace amounts of Cr in water sample.

2. Material and Methods

2.1. Apparatus

The glass column with 10 mm i.d. and 200 mm height was used to make preconcentration column. An UV–Vis spectrophotometer WPA Cambridge UK (Diode Array, Model S2000) was applied for recording the absorption spectra. A spectrophotometer (Perkin-Elmer model 35) with

10mm glass cuvette was used to measure the absorbance at a fixed wavelength. Controlling the reaction temperature was done by a water bath thermostat (Gallenkamp Griffin, BJ-240-V) and a stopwatch was used for recording the reaction time. The synthesis of the TPP-NHCO-SPFGraphene, is illustrated in Fig. 1.

2.2. Reagents

Doubly distilled water and analytical-reagent grade chemicals were used throughout.

2.2.1. Synthesis of TPP-NHCO-SPF Graphene

The first organic-solution-processable functionalized-graphene (SPFGraphene) hybrid material with porphyrins. The synthesis of the porphyrin–Graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together vi a an amide bond (TPP-NHCO-SPF Graphene, Scheme 1 and 2) was carried out using an amine-functionalized prophyrin (TPP-NH$_2$) and Graphene oxide in N,N-dimethylformamide (DMF), following standard chemistry. Large-scale and water-soluble Graphene oxide was prepared by the modified Hummers method[24,25] . Results of atomic force microscopy characterization have confirmed that this grapheme material can be easily dispersed at the state of complete exfoliation, which consists of almost entire single-layered Graphene sheets in H$_2$O[24,25]. TPP-NH$_2$ and Graphene oxide molecules are covalently bonded together by an amide bond. Much care has been taken to make sure all the unreacted TPP-NH$_2$ has been removed using extensive solvent washing, sonication, and membrane filtration. Details are given in the Experimental part. The attachment of organic molecules to Graphene oxide has made TPP-NHCO- SPFGraphene soluble in DMF and other polar solvents[24,26].

2.2.2. Standard Cr solution

A standard solution of Cr(III), 1.0×10^{-3} M was prepared by dissolving 0.1111 g Cr nitrate (Merck) in water containing a drop of concentrated HCl and diluting to the mark in a 250-ml volumetric flask. All working solutions of Cr(III) were prepared by serial dilution of the stock solution.

2.2.3. Standard bromopyrogallol red solution

An aqueous solution of $(1.0 \times 10^{-4}$ M) bromopyrogallol red (Merck) was prepared by dissolving of 0.0140 g bromopyrogallol red in water and diluting to the mark in a 250-ml volumetric flask. Universal buffer solutions in the range from 2.0 to 10.0 were prepared with acetate, phosphate, and borate. Glycine/HCl buffer was used for pH 1.0. Stock solutions (5.0×10^{-3} M) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solutions.

2.3. General procedure

The column was packed with 3.0 g adsorbent and was conditioned with 1.0–2.0 ml of pH 5.0. Then, 10.0 ml of Cr solution (5.0×10^{-5} M) was passed through the column at 0.1 ml min^{-1}. The analyte was eluted from the column by 1.0 ml of HCl, 1.0 M. A sample solution was prepared by pouring 0.5 ml of buffer solution (pH 1.0) in a 10.0 volumetric flask and 3.0 ml of 1.0×10^{-4} M bromopyrogallol red was added. The mixture diluted to ca. 8ml with water

then 1.0 ml of Cr(III) (5.0×10^{-5} M) (eluted solution from column) was added and the solution diluted to the mark with water. The reaction mixture as agitated and then an appropriate amount of the solution was transferred to the spectrophotometric cell and variation in absorbance was recorded for the first 0.5–5.0 min from initiation of the reaction at 517 nm. A calibration graph was plotted with absorbance change ($\Delta A = A_5 - A_{0.5}$) versus Cr concentration.

3. Results and Discussion

Organic-solution-processable functionalized-graphene (SPFGraphene) with the following structure (Scheme 1) is a new chelating agent which can form stable complex with Cr(III). By immobilizing this tridentate bisamide ligand on microcrystalline naphthalene, Cr(III) can be adsorbed. Then desorption of Cr is carried out by using a strong inorganic acid. The Cr(III) concentrations were determined spectrophotometrically after passing solution through the column. Therefore, first the optimum conditions for spectrophotometric procedure should be studied.

3.1. Effect of variables on the determination of Cr

Bromopyrogallol red with following structure Fig. 1 is oxidized by Cr and the absorbance of the solution decreases with time, at $\lambda = 517$ nm. The change in the signal is proportional to Cr concentration. Fig. 3 shows the absorption spectra of bromopyr- ogallol red-Cr system at different times. Experiment (spetrophotometric determination) on eluted Cr solution was done at different pH values (1.0–5.0). Fig. 2 shows the effect of pH on the net absorbance (ΔA). The maximum net absorbance is at pH 1.0; whereas higher pH values cause decreasing in the signal. At higher pH values, oxidation potential of Bromopyrogallol red increases, thus the reaction rate and ΔA decreased. Therefore the pH of 1.0 was selected for this study. The influence of bromopyrogallol red concentration on the reaction rate was tested at pH 1.0 with 1.0×10^{-5} M, Cr(III) at 30 ◦C (Fig. 3). It can be seen that the best concentration for bromopyrogallol red is 3.0×10^{-5} M. At higher values the aggregation of bromopyrogallol red causes the reaction rate to be decreased. Effect of temperature on the maximum signal (ΔA) was studied for the range of 10–50 ◦C, under optimum conditions otherwise as previously described. Fig. 4 shows that with increasing temperature up to 30 °C, ΔA signal or the rate of reaction increases. So temperature was fixed at 30 °C. At higher temperature bromopyrogallol red can be decomposed.

3.2. Effect of variables on the preconcentration

The effect of pH on preconcentration of Cr(III)was examined in range of 1.0–10.0, and the results are shown in Fig. 5. The results show that in the pH range of 5.0–10.0, the analyte was adsorbed on microcrystalline naphthalene quantitate and the recovery was more than 90%. For pH lower than 5.0 the complex will not be formed on adsorbent (at acidic media, active sites of ligand will be protonated) and at high pH values, Cr will precipitate on the column (precipitating instead of adsorption will occur). In order to obtain the best conditions for determination after preconcentration and to prevent the precipitation of Cr (especially at high concentrations), the most acidic pH from this range of buffers (5–10), was selected.
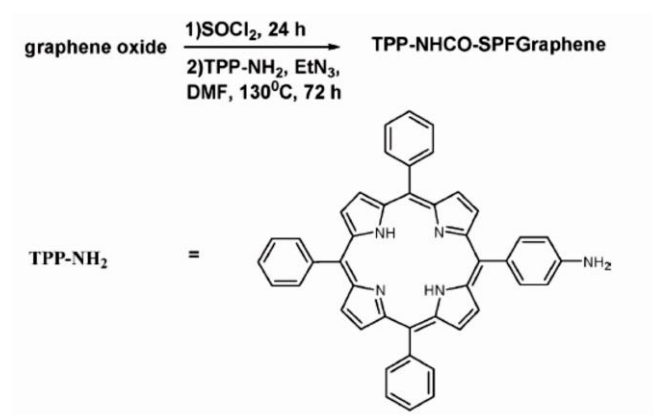
Scheme 1. Synthesis scheme of TPP-NHCO-SPFGraphene [26].
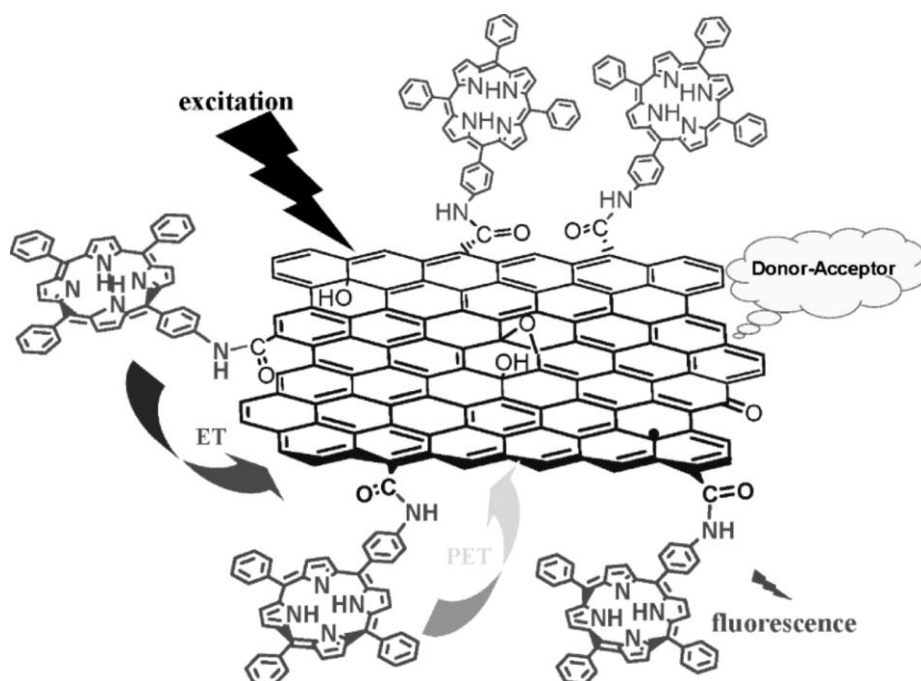
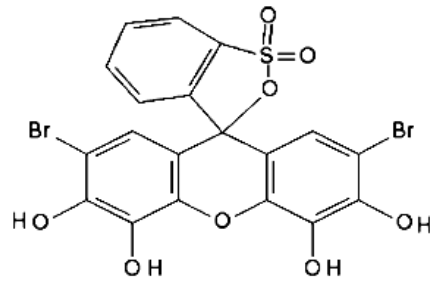**Scheme 2**. Schematic representation of part of the structure of the covalent TPP-NHCO-SPFGraphene[26].
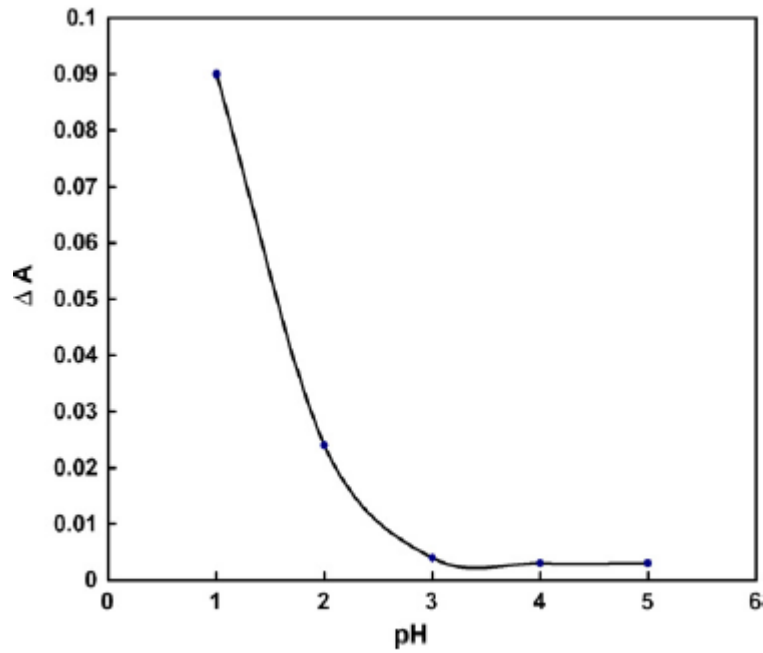
Fig. 1. Structure of Bromopyrogallol red structure.

Fig. 2. Effect of pH on the reaction rate. Conditions: bromopyrogallol red, 1.0×10^{-5} M; Cr(III), 1.0×10^{-5} M; temperature, 30 °C; measuring time, 5.0 min from initiation of the reaction.
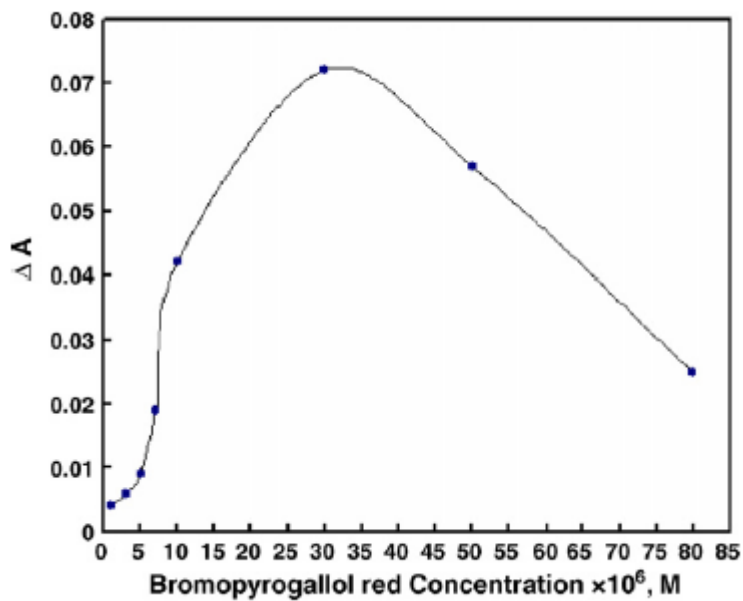

Fig. 3. Effect of bromopyrogallol red concentration on the reaction rate. Conditions: pH 1.0; Cr(III), 1.0×10^{-5}M; temperature, 30 °C; measuring time, 5.0 min from initiation of the reaction.

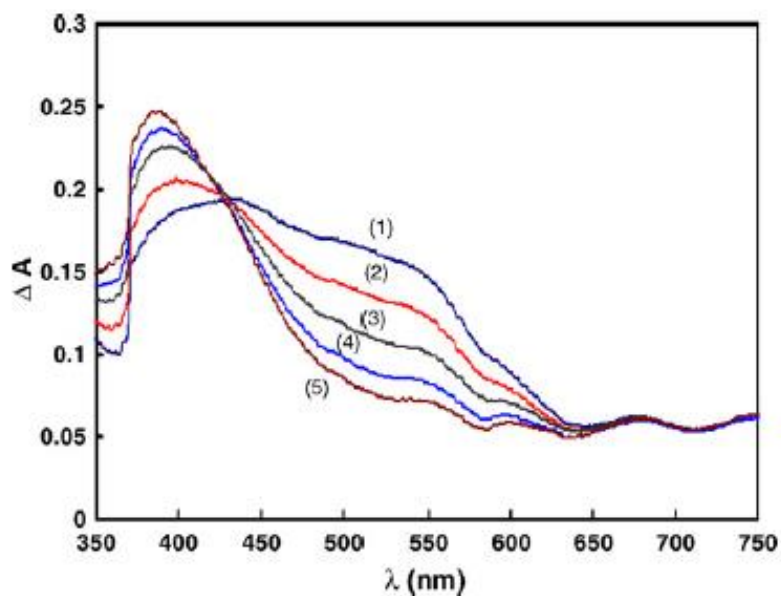**Fig. 4.** Effect of temperature on the rate of reaction. Conditions: pH 1.0; Cr(III), 1.0×10^{-5} M; bromopyrogallol red, 3.0×10^{-5} M; measuring time, 5.0 min from initiation of the reaction.
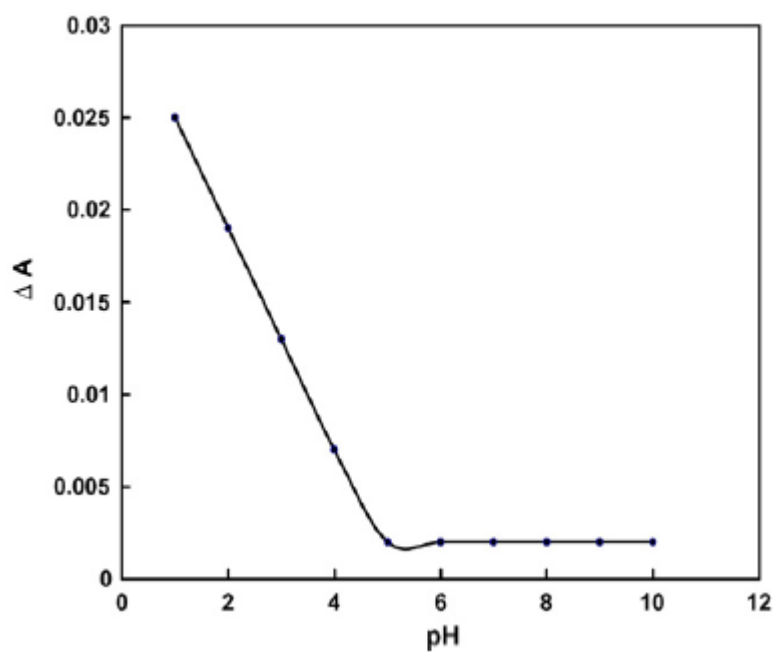

Fig. 5. Effect of pH on the preconcentration recovery. Conditions: Cr(III), 5.0×10^{-6} M; flow rate, 0.1 ml min^{-1}; optimum conditions for determination of Cr(III).
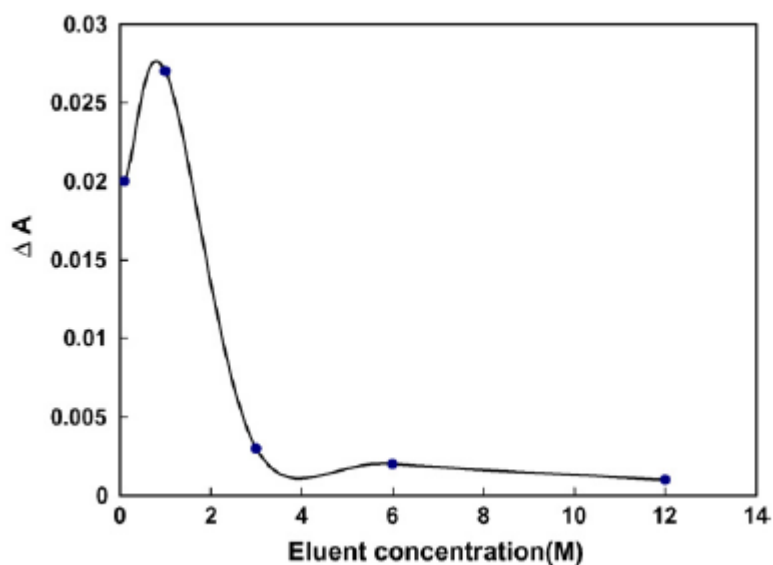
Fig. 6. Effect of HCl concentration for elution. Conditions: Cr(III), 5.0×10^{-6} M; pH 1.0; HCl, 1.0 ml; optimum conditions for determination of Cr(III).

Table 1. Interferences effect on the determination of 5.0×10^{-6} M, Cr(III)

Tolerance limit ($W_{ion}/W_{Cr(III)}$)	Species
100	NH_4^+, Na^+, K^+, H_3BO_3, Hg^{2+}, Ba^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Pb^{2+}, Sn^{2+}, Sr^{2+}, Tl^+
58	Al^{3+}, Mg^{2+}, Cr^{3+}, Cu^{2+}
24	Fe^{2+}, Fe^{3+}
15	Zn^{2+}
1	Sb^{3+}, Ag^+

Table 2. Comparison of some methods for preconcentration and determination of thal-lium with proposed method

Reference	LDR (ng ml^{-1})	DL (ng ml^{-1})	Method
[21]	3.75–17.5	1	Solid–liquid extraction
[22]	0.1–100 5–250	0.08	Potentiometric
[20]		1	stripping
[23]	5–20	4	Liquid–liquid extraction
[24]	40–18000	20	Microcrystalline naphthalene
–	2.1–2000	0.3	Proposed method

Table 3. Determination of Cr(III) in the real samples after preconcentration

Recovery %	ICP	Found ($\times10^{-8}$ M)	Added ($\times10^{-8}$ M)	Sample
–	-	–	–	
98.5	1.05± 0.09	1.09 ± 0.096	1.0	
97.3	4.95 ± 0.08	4.98 ± 0.079	5.0	Drinking water
98.3	8.02 ± 0.10	7.90 ± 0.089	8.0	
97.0	10.41 ± 0.07	10.39 ± 0.016	10.0	
–	–	–	–	
96.6	0.95 ± 0.09	0.99 ± 0.080	1.0	
97.3	4.85 ± 0.08	4.78 ± 0.075	5.0	River water
95.7	7.930 ± 0.00	7.68 ± 0.094	8.0	
98.6	9.95 ± 0.08	10.49 ± 0.076	10.0	

The influence of analyte retention time was investigated by passing 10.0 ml of Cr(III) (5.0×10^{-5} M) solution in the pH 5.0 with different flowrates, and performing the experiment with the passed solution. The results show that in the higher flow rates, Cr cannot be adsorbed on microcrystalline naphthalene quantitavely. The best flow rate was selected to be 0.1 ml min^{-1}. As the Cr complex is unstable in high acidic solutions, hydrochloric acid was selected to desorb the adsorbed analyte. Fig. 6 shows that Cr(III) can be desorbed from the adsorbent by elution with 1.0 ml, HCl, 1.0 M. For investigating the ability of microcrystalline naphthalene to adsorb Cr(III) after sequential elutions, the preconcentration process was repeated for many times. It was indicated that the results were satisfactory, even by using one column for 10 times, without changing the packing. The different volumes of Cr solution, 1.0×10^{-8} M in the range of 10–1000 ml were passed through the column and the signal of each eluted solution was compared with calibration curve data which is achieved from determination method. The obtained signals of concentrated Cr solutions presented that a preconcentration factor of 100 can be achieved by this method. The effect of ionic strength on the sensitivity was studied. The sensitivity would be slightly changed with increasing the ionic strength of the reaction mixture.

3.3. Retention capacity of the adsorbent

The retention capacity of organic-solution-processable functionalized-graphene (SPFGraphene) adsorben was determined by a batch method. The 20 ml solution of Cr(III) 1.0×10^{-4}M in pH 5.0 was transferred in to a separating funnel and 3 g adsorbent was added. The separating funnel was shaken vigorously for 30 min. Concentration of Cr in the filtrate was determined according to calibration curve data and then adsorbed amount of Cr was calculated. The retention capacity (mg adsorbed Cr/ g adsorbent)was obtained to be 0.1672 mg g^{-1}of adsorbent or2.01 mg g^{-1}of ligand.

3.4. Calibration graph, reproducibility and detection limit

A series of standard solutions of Cr(III) were treated under the above mentioned optimized experimental conditions. Cr concentration can be determined in the range of 4.2×10^{-9} to 2.3×10^{-5}M with linear equation; $\Delta A = 0.00078\times C+ 0.0056$ and regression coefficient of $r^2 = 0.9988$ (ΔA is absorbance signal after preconcentration and

C is molar concentration of Cr$\times$106). The experimental limit of detection is 1.42×10^{-9}M (S/N =3). The relative standard deviation (R.S.D.%) for 10 replicate measurements of 5.0×10^{-9}, 1.0×10^{-8}, 1.0×10^{-7}, 3.0×10^{-6} and 1.0×10^{-5}M of Cr(III) were 3.04, 2.95, 2.11, 3.12 and 1.90%, respectively.

3.5. Influence of foreign ions

The influence of contaminant species presented in various samples on the determination of 5.0×10^{-6} M, Cr(III)was investigated. The tolerance limit was defined as the concentration of added ions, causing a relative error less than 3% (Table 1). Some metal cations can be adsorbed on microcrystalline naphthalene at different pH values. This proposed adsorbent is not only able to remove anions of the Cr(III) solution but also can decrease the interference of some cations. Some of important ions that can be found in the real samples with Cr(III) such as Sn^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Pb^{2+} and Tl^{1+} do not have any interference on the determination of Cr(III). Al and Fe can be troublesome in the determination procedure but with preconcentration their interference decreases.

The reported method is selective and simple and it has excellent capacity factor. Among other mentioned methods in Table 2 stripping voltammetry has a good sensitivity but it needs expensive apparatus and needs the operator to be skillful. Conventional solvent extractions are not sensitive enough and they consume a large amount of solvent. Also most of extracting solvents are toxic and volatile. On the basis of the results obtained from the Cr(III) standards, the recommended preconcentration method has been successfully applied prior to spectrophtomeric determination of low values of Cr in the tap water(Tehran, taken after 10 min operation of the tap),rain water(Tehran, 22 January, 2013)samples. The analysiswas performed by using the standard addition technique. The results are summarized in Table 3. Good recoveries in all samples were obtained. This method was reliable through comparing with eachother[32-36].

4. Conclusion

Solid–liquid extraction with microcrystalline naphthalene is an effective separation and preconcentration technique for trace elements. The method has the advantages of being simple, inexpensive and selective This proposed preconcentration method has a high enrichment factor (100) which develops possibility of determining concentration

levels as lowas sub micro amounts of Cr with eliminating the interference of some diverse ions. The selected determination procedure (after preconcentration) is convenient, sensitive and fairly selective.

References

[1]   R.M Izatt., J.S. Bradshaw, S.A.Nielsen, J.D. Lamb, J.J. Christensen (1985) (This Week's Citation Classic), D. Sen, Chem. Rev.85:271-277.

[2]   R.M. Izatt, K.Pawlak, J.S.Bradshaw, R.L. Bruening (1991) (trans-Dichlorido(1,4,8,11-tetraazacyclo-tetradecane)manganese(III) tetrafluoridoborate), Chem. Rev.91:1721-1726.

[3]   R.M. Izatt , K.Pawlak, J.S.Bradshaw, R.L. Bruening (1995) (Self-Assembled Ionophores. An Isoguanosine-K+ Octamer), Chem. Rev.95:2529-2532.

[4]   A.J.Blake, F.Demartin, F.A.Deviallonova, A.Garau, F.Isaia, V.Lippolis, M. Schroder, G. Verani (1996), (Synthesis of dinuclear group 6 metal carbonyl complexes bridged by 4,4′-bipyrazole ligands)J. Chem. Soc., Dalton Trans.3705-3712.

[5]   M.Arca, A.J.Blake, J.Casab, F.Demartin, F.A.Devillanova, A.Garau, F.Isaia, V.Lippolis, R. Kivekas, V.Muns, M.Schroder, G.Verani, (2001)(Conformationally locked pentadentate macrocycles containing the 1,10-phenanthroline unit. Synthesis and crystal structure of 5-oxa-2,8-dithia[9](2,9)-1,10-phenanthrolinophane (L) and its coordination properties to Ni II, Pd II, Pt II, RhIII and Ru II) J. Chem. Soc., Dalton Trans. 1180-1189.

[6]   M.M.Gomes-Gomes, M.M.Hidalgo Garcia, M.A. Palacio Corvillo (1995) (On-line preconcentration of silver on a sulfhydryl cotton microcolumn and determination by flow injection atomic absorption spectrometry), Analyst120:1911-1916.]

[7]   S.P.Boudreau, W.T. Cooper (1989)(Analysis of thermally and chemically modified silica gels by heterogeneous gas-solid chromatography and infrared spectroscopy), Anal. Chem.61:41-47.

[8]   M.E. Mahmoud (1997),(Silica gel-immobilized Eriochrome black-T as a potential solid phase extractor for zinc (II) and magnesium (II) from calcium (II)) Talanta 45: 309-314.

[9]   M.E. Mahmoud (1997) (Study of the selective extraction of iron (III) by silica-immobilized 5-formyl-3-arylazo-salicylic acid derivatives)Talanta. (1997) Talanta 44: 15-21.

[10]   M.E Mahmoud., E.M. Soliman (1997) (Study of the selective extraction of iron (III) by silica-immobilized 5-formyl-3-arylazo-salicylic acid derivatives), Talanta 44 :1063-1071.

[11]   E.M. Mahmoud (1999) (Selective solid phase extraction of mercury(II) by silica gel-immobilized-dithiocarbamate derivatives), Anal. Chim. Acta 398: 297-302.

[12]   M.E. Mahmoud (1998), in: Proceeding of the 25th FACSS Conference, Austin, TX, USA, 11–15 October.

[13]   A.Tong, Y.Akama, S.Tanaka (1990) (Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay), Anal. Chim. Acta 230: 179-185.

[14]   A.Moghimi, R.Ghiasi, A.R. Abedin, S Ghammamy. (2009) (Solid phase extraction of Cd(II) using mesoporous organosilicas and determination by FAAS) ,African Journal of Pure and Applied Chemistry,3 (3): 051-059.

[15]   A. Moghimi, (2007), (Preconcentration and Determination of Trace Amounts of Heavy Metals in Water Samples Using Membrane Disk and Flame Atomic Absorption Spectrometry),Chinese Journal of Chemistry, 25(10): 640-645.

[16]   A.Moghimi, M.S. Tehrani., S. Waqif Husain (2006)(Preconcentration and Determination of Copper(II) Using Octadecyl Silica Membrane Disks Modified by 1,5-Diphenylcarhazide and Flame Atomic Absorption Spectrometry), Material Science Research India 3(1a): 27-32.

[17]   A,Moghimi, M. Abdouss (2012) Preconcentration of Ni(II) from sample water by modified poly (ethylene terephthalate)-grafted-acrylic acid/acryl amide fiber), Afr. J. Pure Appl. Chem. 6(8):110-118.

[18]   H.Wang, H.S.Zhang, J.K. Cheng (1999)(Studies on 2-(2-thiazolylazo)-5-diethylaminophenol as a precolumn derivatizing reagent in the separation of platinum group metals by high performance liquid chromatography), Talanta 48:1-8.

[19]   M.Zargaran, A. M.Shoushtari, M.Abdouss (2008) (Ion adsorption studies of micro and nano acrylic fibers modified by ethanolamine. Ionen Adsorption von mit Ethanolamin modifizierten Mikro- und Nano-Acylfasern), J. Appl. Polym. Sci, 110:3843-3849.

[20]   M.Tabarzadi, M. Abdouss, S. A.Hasani, A.M.Shoushtary, U.Mat.-wiss. (2010)(Ion adsorption studies of micro and nano acrylic fibers modified by ethanolamine. Ionen Adsorption von mit Ethanolamin modifizierten Mikro- und Nano-Acylfasern)Werkstofftech. 41(4):221-228.

[21]   D. H.Shin, Y. G.Ko, U. S. Choi, W. N. Kim (2004) (Fluorescence Enhancement of Coumarin Thiourea Derivatives by Hg^{2+}, Ag^+, and Silver Nanoparticles), Ind. Eng. Res. 43: 2060-2065.

[22]   P.Nayebi, , A.Moghimi , (2006) (Perconcentration and Determination of copper(II) by 1-(2- Pyridyl Azo)2-Naphtol(PAN) modified Octadecyl Silica),Oriental Journal of Chemistry,22(3):507-512.

[23]   O. R. Hashemi, K. M.argar-Razi, F. Raoufi, A. Moghimi, H. Aghabozorg, M. R.Ganjali, (Ultra-trace monitoring of copper in environmental and biological samples by inductively coupled plasma atomic emission spectrometry after separation and preconcentration by using octadecyl silica

membrane disks modified by a new schiff's base) (2001). Microchemistry Journal. 69:1-8.

[24]   M. R. Ganjali, M. R. Pourjavid, L. H. Babaei, M. S. Niasari. (2004). (Octadecyl Silica Membrane Disks Modified with a New Schiff's Base for the Preconcentration of Lead and Copper before Their Determination in Water Samples) Quim Nova. 27: 213.

[25]   A. Moghimi, M. Shabanzadeh. (2012). (Extraction and Determination of Trace Copper (II) Using Octadecyl SilicaMembrane Disks Modified 1-(2-Pyridyl Azo) 2-Naphtol(Pan) in Water Samples and Paraffin-Embedded Tissues from Liver Loggerhead Turtles Specimens by FAAS) Journal of Chemical Health Risks. 2(2):7-16.

[26]   C. Tang, A. Tracz, M. Kruk, R. Zhang, D.-M. Smilgies, K. Matyjaszewski, T. Kowalewski. (2005). High-Performance Poly(3-hexylthiophene) Field-Effect Transistors Fabricated by a Slide-Coating Method. Journal of American Chemical Society. 127:6918.