Artigo

Quim. Nova, Vol. 29, No. 3, 440-443, 2006

A NOVEL METHOD FOR FAST ENRICHMENT AND MONITORING OF HEXAVALENT AND TRIVALENT CHROMIUM AT THE PPT LEVEL WITH MODIFIED SILICA MCM-41 AND ITS DETERMINATION BY INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

Mohammad Reza Ganjali*, Leila Hajiagha Babaei, Alireza Badiei and Kamal Saberian
Department of Chemistry, Tehran University, Tehran, Iran
Seiedmahmoudreza Behbahani
Abureihan Higher Education Complex, Department of AgriculturalMachinery Technology, Tehran University, Tehran, Iran
Ghodsi Mohammadi Ziarani
Department of Chemistry, Alzahra University, Tehran, Iran
Masoud Salavati- Niasari
Department of Chemistry, Kashan University, Kashan, Iran

Recebido em 12/1/05; aceito em 25/8/05; publicado na web em 16/2/06

Chromium(III) at the ng L^{-1} level was extracted using partially silylated MCM-41 modified by a tetraazamacrocyclic compound (TAMC) and determined by inductively coupled plasma optical emision spectrometry (ICP OES). The extraction time and efficiency, pH and flow rate, type and minimum amount of stripping acid, and break- through volume were investigated. The method's enrichment factor and detection limit are 300 and 45.5 pg mL^{-1}, respectively. The maximum capacity of the 10 mg of modified silylated MCM-41 was found to be 400.5±4.7 µg for Cr(III). The method was applied to the determination of Cr(III) and Cr(VI) in the wastewater of the chromium electroplating industry and in environmental and biological samples (black tea, hot and black pepper).

Keywords: chromium; modified MCM-41; ICP OES.

INTRODUCTION

In recent years, the determination of chromium has received considerable attention. Chromium is usually found in natural waters in two different oxidation states, Cr(VI) and Cr(III). Both forms of chromium enter to the environment from various sources at the effluent discharge of tanning industries, electroplating, oxidative dying, cooling water power, chemical industry and steel works[1,2]. Depending on its oxidation state, the physiological effects of chromium on the biological systems are totally opposite. Chromium (III) is considered an essential element in mammals for the maintenance of glucose, lipid and protein metabolism, whereas Cr (VI) is considered to be a toxic material[1,3,4], because of its ability to oxidize other species and its adverse impact on lung, liver and kidney. Owing to these two contrary effects, the precisely accurate determination of both species is essential. Due to the different properties and toxicity of the chemical forms of chromium, a great number of speciation studies have been performed[5].

The direct determination of chromium in water may not be possible with sufficient sensitivity by also expensive analytical methods such as inductively coupled plasma atomic optical spectrometry (ICP OES)[6] or electrothermal atomic absorption spectrometry (ETAAS)[1] because of low concentrations and/or matrix interferences. For this purpose, various separation and pre-concentration methods such as liquid-liquid extraction[1,6], coprecipitation[3,7], ion exchange[8-10] and adsorption[11-14] have been developed. Sugiyama *et al.*[6] determined trace elements including chromium in natural waters by ICP OES after preconcentration by dithiocarbamate extraction. Subramainan[1] developed a procedure using APCD–MIBK (Ammonium pyrrolidinedithiocarbamate – Methylisobutyl ketone) extraction system for the determination of Cr(III) and Cr(VI) by ETAAS. Isshiki *et al.*[11] used macroporous polystyrenedivinylbenzene as an adsorbent for the preconcentration of chromium species. Demirata *et al.* used melamine-formaldehyde for the same purposes[13]. Morocco et al. proposed a procedure for the preconcentration of Cr(VI) with tributyltin chloride immobilized on C18 film[14]. Some of these adsorbents may be fairly effective for pre-concentration by sorption of metal ions, but their methods of preparation are lengthy and involve rigid control of conditions.

The synthesis of a new form of mesoporus silica molecular sieves[15,16], preparated using surfactants as organic templates, initiated a new field of research in material science. Among them, MCM-41 is the most studied. It possesses a uniform hexagonal array of linear channels constructed with a silica matrix like a honeycamb. The diameter of their channels can be tailored by using surfactants with different molecular size. Due to high surface area and large channel diameters, these materials attract much attention as a new host for large molecules[17-19].

The major advantages of the modified MCM-41 include (1) very short sample processing time, 2 min, due to the warm like of particles which allows the sample processing at very higher flow rates, (2) reduced channeling resulting from the use of uniform diameter sorbent with same length, 10 mm, and a greater mechanical stability of the sorbent.

In this work, we wish to introduce a novel method for fast separation, preconcentration and ICP OES determination of ultra trace amounts of chromium in both states in biological, environmental and industrial samples. To the best our knowledge, this is the first application of modified MCM-41 with tetraazamacrocyclic compound (Figure 1) for separation and preconcentration of ultra trace amounts of chromium.

---

*e-mail: Ganjali@khayam.ut.ac.ir

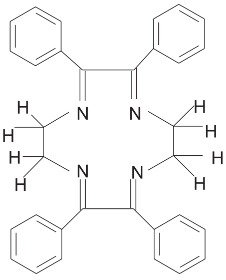

Figure 1. *Structure of TAMC*

EXPERIMENTAL PART

Reagents

Fumed silica (Cab-O-Sil Degussa), sodium silicate (Aldrich), and TMA-silicate (Sachem) were used for synthesis of silylated MCM-41. All organic solvents (HPLC grade) were from Merck Chemical Company. All acids used were of the highest purity available from Merck. Analytical grade nitrate salts of lead, sodium, potassium, magnesium, calcium, strontium, nickel, cadmium, copper and chromium (all from Merck) were of the highest purity available and used without any further purification. Doubly distilled deionized water was used throughout. The TAMC (tetraazomacrocyclic compound) was synthesized and purified as described elsewhere[20].

Synthesis of silylated MCM-41

The MCM-41 was synthesized according to litrature[21,22] using a gel composition (in mol) of 100 SiO_2, 8.64 Na_2O, 4.38 $(TMA)_2O$, 31.24 CTMABr, and 6330 H_2O (TMA^+= tetramethylammonium and CTMABr=cetyltrimethylammonium bromide). A clear gel was obtained after 10 min of stirring a mixture containing fumed silica (Cab-O-Sil Degussa), sodium silicate, and TMA-silicate in water. The addition of CTMABr was followed by vigorous stirring for 60 min. The so-obtained dense foam was maintained for 24 h at 100 ºC in a Teflon-lined static autoclave. A white solid was filtered off and dried in air. A mass of 1.0 g of solid was treated under reflux at 100 °C in 20 ml of a 1:1 mixure of hexamethyldisilazane and hexamethyldisiloxane (HMDSO) for one night. The silylated MCM-41 was washed with ethanol and dried in air. The surfactant was removed from solid by HCl 0.1 mol L^{-1} in ethanol[23].

Modification of silylated MCM-41

100 mg of TAMC was dissolved in 5 mL chloroform and then 20 mg of silylated MCM-41 was added to the solution and the mixture was stirred for 5 min. The resulting mixture was dried in air.

Apparatus

The chromium and other cations determination were carried out by ICP OES varian, model LIDERTY 150 AX Turbo.

Ultra trace amounts of chromium ion were determined by Gama spectrometry, Silena-Italy with HPGE detector. The XRD (X-ray Diffraction) was obtained from Siemens D500 diffractometer employing nickel filtrated CuKα (λ = 1.5418 ºA). The specific surface was determined from the linear part of BET plot (p/p_o=0.05 – 0.03) at 77 K using Omnisorb 100.

Sample extraction

The general procedure for extraction of Cr(III) ions by the modified MCM-41 was as follows. To 100 mL of the sample solution containing 2 µg Cr(III), 10 mg of modified MCM-41 was added and the mixture was stirred for at least 2 min. Then, the resulting mixture was filterated on a paper filter.The extracted Cr(III) on the paper, was then stripped using 10 mL of 3.0 mol l^{-1} solution of nitric acid into 10 mL volumetric flask and the chromium concentration was determined by ICP OES.

For separation and determination Cr(VI) must be coverted to Cr(III). Thus, before extraction, addition of 0.1 mL of sodium thiosulfate (0.1 mol L^{-1}) to the solution is necessary. At first Cr(III) is determined after addition of sodium thiosulfate solution, Cr(VI) is reduced to Cr(III) and subsequently determined as total chromium; the difference gives the Cr(VI) present in sample.

RESULTS AND DISCUSSION

The XRD pattern of acid silylated MCM-41 washed reflects the high quality of hexagonal array[15]. The final product showed the BET surface area 800 m^2/g and pore diameter 28 ºA, based on adsorption-desorption of N_2 at 77 ºK.

The tetraazamacrocyclic compound (TAMC) with a rigid cavity and sufficient lipophilicity can form very selective complex with Cr(III) ion[24], and it was used as an excellent ionophore in construction of a highly selective and sensitive Cr(III) membrane sensor[24]. Thus, we were interested to consider its ability as a suitable modifier for silylated MCM-41 in separation and pre-concentration of Cr(III) in different samples.

At the first, experiments were carried out in order to choose a proper eluent for the retained chromium after the extraction of 1 µg Cr(III) in 100 ml solution by the modified MCM-41, Chromium(III) was stripped with common inorganic and organic acids and results are given in Table 1. The data given in Table 1, revealed that among four different acid solutions used, 10 mL of 3.0 mol L^{-1} nitric acid can accomplish the quantitative elution of Cr(III) from the modified MCM-41, while other acids used are ineffective for the complete elution of Cr(III) from the modified MCM-41.

Table 1. Recovery of Cr(III) from the modified MCM-41 using different stripping acid solutions[a]

Stripping acid solution	Volume (mL)	% Recovery of Cr (III)
(3 mol L^{-1})		
HNO_3	20	99.9 (0.5)[b]
HNO_3	10	99.8 (0.7)
HNO_3	5	89.2 (0.8)
HOAc	10	72.7 (1.2)
HBr	10	76.6 (1.1)
HCl	10	71.1 (0.9)

[a] Initial samples contained 2 µg Cr(III) in 100 mL water; [b] RSD based on three replicate analysis

In solid phase extraction, the extraction rate is very important. Thus, the effect of flow rates on extraction efficiency of the sample solution from the modified MCM-41 for the Cr(III) ion was investigated. It was found that, in the range of 20-200 mL min^{-1}, the retention of Cr(III) by the modified MCM-41 is not affected by the sample solution flow rate. It should be noted that, this method is one of the faster method in solid phase extraction of cations from aqueous samples.

The influence of extraction time on efficiency of extraction for a series of solutions containing 2 µg of chromium was studied and the results showed that the time of extraction (from 2 to 60 min) has not any effect on extraction efficiency of the ions.

To investigate the optimum amount of modified MCM-41 on the quantitative extraction of chromium, the extraction was conducted by varying amounts of the modified MCM-41 from 2-20 mg, and the results are summarized in Table 2. As it is obvious, the extraction of chromium is quantitative by using 10 mg of modified MCM-41. Hence, subsequent extraction experiments were carried out with 10 mg of modified MCM-41.

Table 2. Effect of amount modified MCM-41 on recovery of Cr(III) ion[a]

Modified MCM-41 (mg)	% Extraction of Cr(III)
2	20.5 (1.1)
4	41.2 (1.0)
6	66.3 (0.5)
8	91.2 (0.5)
10	99.9 (0.9)
20	99.1 (0.7)

[a] Initial samples contained 2 µg Cr(III) in 100 mL water; [b] RSD based on three replicate analysis

The effect of pH of aqueous samples on the extraction of 2 µg Cr(III) from 100 mL solution was investigated in the range 2.0 to 10.0 (the pH was adjusted by using 0.1 mol L^{-1}of either nitric acid or sodium hydroxide solutions). The results are depicted in Figure 2. As it can be seen from Figure 2, the quantitative extraction of Cr(III) by the modified MCM-41 is independent of pH in the range 4.0-10.0. At lower pH (< 4.0), the nitrogen atoms of the TAMC could be some protonated and reduced the stability of complex formation between TAMC and Cr(III) ion.

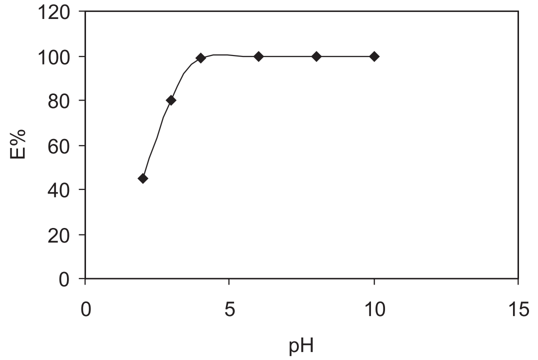

Figure 2. *The effect of pH of the aqueous samples on the extraction of Cr(III)*

The break-through volume of the sample solution was tested by dissolving 2 µg of the chromium in 100, 250, 500, 1000, 2000, 2500 and 3000 mL of water, and the recommended procedure was followed. In all cases, the extraction by modified membrane MCM-41 was found to be quantitative. Thus the break-through volume for the method should be greater than 3000 mL.

The limit of detection (LOD) and limit of quantification (LOQ) of the proposed method for the determination of chromium ion were studied under the optimal experimental conditions. The LOD and LOQ obtained[25,26] from $C_{LOD}=K_bS_bm^{-1}$ and $C_{LOQ}=K_aS_bm^{-1}$ (S_b is the standard deviation blank solution and m is the slope of calibration curve) for a numerical factor $K_b=3$ and $K_a=10$, and concentration factor of 300 are 45.5 pg mL^{-1}and 151.7 pg mL^{-1} respectively.

The maximum capacity of the 10 mg modified MCM-41 was determined by passing 100 mL portions of an aqueous solution containing 1000 µg chromium through the modified MCM-41, followed by determination of the retained chromium ions using ICP OES. The maximum capacity was found to be 400.5±4.7 µg of chromium.

Separation and determination of chromium in binary mixtures

In order to investigate the selective separation and determination of chromium ions from water containing diverse metal ions, an aliquot of aqueous solution (100 ml) containing 1 µg chromium and various amounts of other cations was taken and the recommended procedure was followed, and the results are summarized in Table 3. The results show that, the chromium ions in the binary mixtures are retained almost completely by the modified MCM-41.

Table 3. Extraction of Cr(III) and Cr(VI) from binary mixtures[a]

Diverse ion	Amount taken (µg)	% Extraction of Cr(III)	% Extraction of Cr(VI)
Na^+	100000	99.7 (0.4)	99.8 (1.4)[b]
K^+	100000	99.9 (0.5)	99.6 (1.0)
Mg^{2+}	100000	100.0 (0.9)	100.0 (1.2)
Ca^{2+}	100000	100.2 (0.8)	99.9 (1.1)
Sr^{2+}	100000	100.0 (1.2)	100.1 (1.0)
Cd^{2+}	5000	99.9 (0.7)	99.6 (1.2)
Ni^{2+}	5000	99.8 (0.5)	99.8 (1.0)
Cu^{2+}	5000	100.0 (0.9)	99.7 (1.2)
Pb^{+2}	5000	99.7 (0.7)	100.0 (0.8)

[a] Initial samples contained 1 µg Cr(III) and 1 µg Cr(VI) in 100 mL water; [b] RSD based on three replicate analysis

Speciation of Cr(III) and Cr(VI) in wastewater

The proposed method was used for speciation of both case of chromium in two different wastewater samples (Electroplatig factory, Tehran, Iran), and the results are given in Table 4. As it can be seen, the results obtained by the proposed method and Gama Spectrometry are in satisfactory agreement.

Table 4. Determination of hexavalent and trivalent chromium in wastewater samples

Sample	Cr(III) (ng g^{-1})		Cr(VI) (ng g^{-1})	
	SPE-ICP OES	G-S	SPE-ICP OES	G-S
1	1.7 (0.4)[a]	1.5 (0.5)	109.5 (0.9)	109.0 (0.7)
2	2.2 (0.3)	2.1 (0.4)	191.9 (0.8)	192.2 (0.7)

[a] RSD based on three replicate analysis

Determination of chromium in black tea

The proposed method was also applied to determination of chromium in two black tea samples. The procedure used for the extraction of cations from samples was similar to that reported in the literature[27]. 100 mg of dry sample (dried at 110 °C) was placed in a 50 mL beaker, followed by the addition of 7 mL of concentrated nitric acid, and the beaker was covered with a glass watch. The beaker was allowed to stand over night, and the contents were heated on a hot plate (150 °C for 15 min). Then the sample was cooled, 8 mL of perchloric acid was added, and the mixture was heated again at 200 °C until the solution became clear (about 1 h). The glass watch was removed and the acid evaporated to dryness at 250 °C. The white residue was completely dissolved in 5 mL of 1 mol L^{-1} nitric acid and the solution was transferred to a 100 mL calibrated flask. 0.1 mL sodium thiosulfate (0.1 mol L^{-1}) was added to this solution, and then, the solution was neutralized with a proper NaOH solution and the solution was diluted to the mark, and the recommended procedure was followed. The results are shown in Table 5. As it can be seen, the amount of the total chromium in black tea samples can be accurately determined with the proposed method.

Table 5. Determination of total chromium in black tea, hot and black pepper samples

Sample	Cr(III) (ng g^{-1})		Cr(VI) (ng g^{-1})	
	SPE-ICP OES	G-S	SPE-ICP OES	G-S
Iranian black tea (Lahijan)	3.68 (0.5)[a]	3.57(0.4)	0.04(0.02)	0.03(0.01)
Indian black tea (Seylon)	3.35 (0.3)	3.50(0.3)	0.05(0.02)	0.05(0.02)
Black pepper	6.88 (0.8)	6.52(0.7)	0.07(0.03)	0.08(0.03)
Hot pepper	8.47 (0.5)	8.41(0.5)	0.09(0.03)	0.09(0.02)

[a] RSD based on three replicate analysis

Determination of chromium in black and hot pepper

A 10 mg pepper was taken in a beaker and dissolved in concentrated nitric acid (5 mL) with heating. The solution was cooled, neutralized with NaOH solution, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. An aliquot (10-20 mL) of the sample solution was taken and the total chromium was determined by the general procedure. The results are given in Table 5. As it can be seen the results obtained by the proposed method and Gama Spectrometry are in satisfactory agreement.

Comparison of the proposed method with the previously reported methods

Table 6 compares the performance characteristics of the proposed method, with those of the previously reported pre-concentration methods. As it is obvious, the proposed method not only in the term of the concentration factor, but also in the terms of detection limit and the extraction rate, are superior to those previously reported.

Table 6. Comparison of concentration factor, detection limit, and extraction rate of the propose method and the best reported methods

Method	Concentration Factor	Detection limit (µg L^{-1})	Extraction rate (µL min^{-1})	Ref.
1	25	45	1.5	28
2	-	500	3.5	29
3	-	2	3.4	30
4	50	2.5	(10 min)	31
5 Cr(III)	86	0.025	2.5	32
Cr(VI)	50	0.020	2.5	-
This work	300	0.045	(5 min)	-

CONCLUSIONS

The proposed method has the following advantages: The method is fast, it can selectively separate Cr(III) ions from other metal ions associated, even much higher concentrations, and it can be successfully applied to separation, speciation and determination of ultra trace amounts of Cr(III) and Cr(VI) (45.5 pg mL^{-1}) using partial silylated MCM-41 modified by tetraazamacrocyclic compound and ICP OES. The method was used for determination of Cr(III) and Cr(VI) in industrial, biological and environmental samples.

ACKNOWLWGGEMENTS

The author thanks the Tehran University Research Council for support of this work.

REFERENCES

1. Subramanian, K. S.; *Anal. Chem*. **1988**, *60*, 11.
2. Sperling, M.; Xu, S.; Welz, B.; *Anal. Chem*. **1992**, *64*, 3101.
3. Lan, C. R.; Tseng, C. L.; Yang, M. H.; *Analyst* **1991**, *116*, 35.
4. Gaspar, A.; Posta, J.; Toth, R.; *J. Anal. At. Spectrom*. **1996**, *11*, 1067.
5. Nusko, R.; Heuman, K. G.; *Fresenius J. Anal. Chem.* **1997**, *357*, 1050.
6. Sugiyama, M.; Fujino, O.; Kihara, S.; Matsui, M.; *Anal. Chim. Acta* **1986**, *181*, 159.
7. Boughriet, A.; Deram, L.; Wartel, M.; *J. Anal. At. Spectrom*. **1994**, *9*, 1135.
8. Johnson, C. A.; *Anal. Chim. Acta* **1990**, *238*, 273.
9. Milac¡ic, R.; Stupar, J.; Koz¡uh, N.; Koros¡in, J.; *Analyst* **1992**, *117*, 125.
10. Yoshimura, K.; *Analyst* **1988**, *113*, 471.
11. Isshiki, K.; Sohrin, Y.; Karatani, H.; Nakayama, E.; *Anal. Chim. Acta* **1989**, *224*, 55.
12. Bag, H.; Turker, A.R.; Lale, M.; Tunceli, A.; *Talanta* **2000**, *51*, 895.
13. Demirata, B.; Tor, I.; Filik, H.; Afsar, H.; *Fresenius J. Anal. Chem*. **1996**, *356*, 375.
14. Morocco, M. T.; Newman, G. P.; Syty, A.; *J. Anal. At. Spectrom*. **1990**, *5*, 29.
15. Kresge, C. T.; Leonowicz, N. E.; Vartuli, J. C.; Roth, W. J.; Beck, J. S.; *Nature* **1992**, *359*, 710.
16. Beck, J. S.; Vartuli, J. C.; Roth, W.J.; Leonowicz, N.E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Scheppard, E. W.; McCullem, C. B.; Higgins, J. B.; Schlenker, J. L.; *J. Am. Chem. Soc.* **1992**, *114*, 10834.
17. Brunel, D.; Bellocq, N.; Sutra, P.; Cauvel, A.; Lasperas, M.; Moreau, P.; DiRenzo, F.; Galarneau, A.; Fajula, F.; *Coord. Chem. Rev*. **1998**, *178*, 1085.
18. Sorokin, A. B.; Tuel, A.; *Catal. Today* **2000**, *57*, 45.
19. Corriu, R. J. P.; Lancelle-Beltran, E.; Mehdi, A.; Reye, C.; Brandes, S.; Guilard, R.; *J. Mater. Chem*. 2002, *12*, 1355.
20. Varshiney, A.; Tandon, J. P.; *Polyhedron* **1986**, *5*, 1853.
21. Reddy, K. M.; Song, C.; *Catal. Lett.* **1996**, *36*, 103.
22. Badiei, A.; Bonneviot, L.; *Inorg. Chem.* **1998**, *37*, 4142.
23. Badiei, A.; Cantournet, S.; Morin, M.; Bonneviot, L.; *Langmuir* **1998**, *14*, 7087.
24. Ganjali, M. R.; Mizani, F.; Salavati-Niasari, M.; Javanbakht, M.; *Anal. Sci.* **2003**, *19*, 235.
25. ACS Committee on Enviromental Improvement; *Anal. Chem*. **1980**, *52*, 2242.
26. Ingle, J. D.; Crouch, S. R.; *Spectrochemical Analysis*, Prentice Hall: Englewood Cliffs, NJ, 1988.
27. Ichinoki, S.; Yamazaki, M.; *Anal. Chem*. **1985**, *57*, 2219.
28. Tunceli, A.; Rehber, T. A.; *Talanta* **2002**, *57*, 1199.
29. Kubota, L. T; Gushikem, Y.; *Analyst* **1991**, *116*, 281.
30. Peixoto, C. R. M.; Gushikem, Y.; Baccan, N.; *Analyst* **1992**, *117*, 1029.
31. Soylak, M.; Divrikli, U.; Elci, L.; Dogan, M.; *Talanta* **2002**, *56*, 565.
32. Posta, J.; Gaspar, A.; Toth, R.; Ombodi, L.; *Microchem. J.* **1996**, *54*, 195.