Fabrication of NanoGraphene by new method Separation of Trace Amounts of Mo^{2+} in Water Samples Using

Ali Moghimi
Department of Chemistry, Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran

Abstract

A new sensitive and simple method was developed for the pre concentration of trace amounts of Mo using 1-(2-pyridylazo)-2-naphthol (PAN) as chelating reagent prior to its determination by flame atomic absorption spectrometry. The proposed method is based on the uti- lization of a column packed with graphene as sorbent. Several effective parameters on the extraction and complex formation were selected and optimized. Under optimum conditions, the calibration graph was linear in the concentration range   of 5.0–240.0 µg L^{-1} with a detection limit of 0.36 µg L^{-1}. The relative standard deviation for ten replicate measurements   of   20.0 and 100.0 µg L^{-1} ofMo were 3.45 and 3.18%, respectively. Comparative studies showed that graphene is superior to other adsorbents including C$_{18}$ silica, graphitic carbon, and single- and multi-walled carbon nanotubes for the extraction ofMo. The proposed method was successfully applied in the analysis of four real environmental water samples good   spiked recoveries over the range of 95.8–98.6% were obtained.

Keyword: Graphene; Solid-phase extraction; Preconcentration; Flame atomic absorption spectrometry; Mo

1. Introduction

Mo at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems [1-8].This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Mo can bind to the cell membrane and hinder the transport process through the cell wall. Mo at nearly 40ng mL^{-1} is required for normal metabolism of many living organisms [9, 10.] On the other hand, Mo 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 Mo is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) [11, 12] as well as spectrometric methods [13, 14] .

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 [18-19,35]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].

To ease the retrieval procedure, the SPE using graphene as the absorbent in a column combined with flame atomic absorption spectrometry (FAAS) has been demonstrated by our research group [36]. We extend its application to other inorganic analyses. 1-(2-Pyridylazo)-2-naphthol (PAN), a chelating agent which forms stable complexes with a number of metals and has found numerous applications in trace element separation and pre-concentration methods [37], was used to extract Co (structure of the Mo-PAN complex is shown in Fig. 1). What is more, it possesses a benzene ring structure. Based on this, the Mo-PAN is considered to have formed a strong p-stacking interaction with graphene when the sample solution passes through the column during which the Mo- chelate is retained. The factors influencing the efficiency of SPE and FAAS determinationwere systematically studied. The proposed method has been applied for the determinationof trace amounts of Mo in water samples with satisfactory results. It reveals great potential of graphene as an excellent sorbent material in analytical processes for metal ions once again
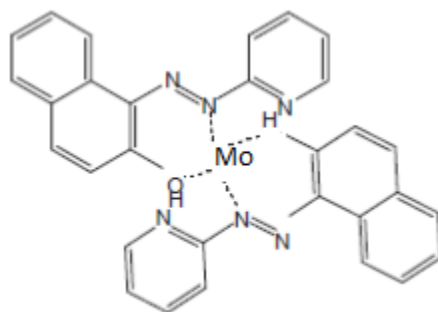
Figure 1. Structural formulae of the Mo-PAN complex.

2. Experimental

2.1. Apparatus

A Shimadzu (Kyoto, Japan) Model AA-6300C atomic absorption spectrometer equipped with deuterium background correction and a Mo hollow-cathode lamp as the radiation source were used for absorbance measurements   at a wavelength of 240.7 nm. All measurements werecarried out in an air/acetylene flame. The instrumental parameters were adjusted according to the manufacturer's recommendations. A pH3-3C digital pH meter equipped with a combined glass–calomel electrode (Hangzhou Dongxing Instrument Factory,   Hangzhou, China)   was used for pH adjustment. The SPE experiments were performed on an Agilent vacuum manifold processing station with a Gast vacuum pump (Tegent Technology Ltd. Shanghai, China). The empty SPE columns (3.0 mL) and SPE frits were purchased from Agilent.

2.2. Reagents and materials

Graphite powder (50 mesh), potassium   permanganate ($KMnO_4$), concentrated sulfuric acid (H_2SO_4), and sodium nitrate ($NaNO_3$) were purchased from Tianjin Tianda Chemical Reagent Company (Tianjin, China). A stock standard solution of Mo at a concentration of 1000 µg mL^{-1} was purchased from the National Institute of Standards (Beijing, China). Working standard solutions were prepared daily through serial dilutions of the stock solution with deionized water prior to analysis. The chelating agent, 2.0 g L^{-1} PAN solution, was preparedby dissolving the appropriate amount   of PAN (ShanghaiChemistry Reagent Company, Shanghai, China) in absolute ethanol. Stock solution of diverse elements was prepared from high purity compounds. Single-walled CNTs (SWCNTs, carbon purity >90%, outer diameter <2 nm, length 5–15 µm) and multi-walled CNTs (MWCNTs, carbon purity >98%, outer diameter 20–40 nm, length 5–15 µm) were obtained from the Beijing Chemistry Reagent Company (Beijing, China).The GO was synthesized according to the modification of Hummers' methods[47].
Nitric acid (0.1 mol.L^{-1}) was used to adjust the pH in the2–3 range, and ammonium acetate buffers (0.2 mol.L^{-1}) were prepared   by adding   an appropriate amount   of acetic acid toammonium acetate solutions resulting in solutions with a pH range of 4.0–5.0. For a pH range of 6.0–8.0, a phosphate buffer solution   (0.2 mol.L^{-1})   was prepared   by adding   an

appropriate amount of disodium hydrogen phosphate to sodium hydrogen phosphate. Ammonium chloride buffer solutions (0.2 mol.L^{-1}) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions, resulting in solutions with a pH range of 9.0–10.0.All reagents used were of analytical reagent grade. Deionized water was used in the preparation of all solutions. All glassware and columns were kept in 10% nitric acid for at least24 h and subsequently washed four times with deionized water before application.

2.3. Synthesis and characterization of graphene

Graphene nanoparticles were synthesized according to our previously reported study[36]. The size and morphology of G was observed by scanning electron micros- copy (SEM) using an S-3000N microscope and X-ray diffraction (XRD) measurement was carried out using a Rigaku D/ max-rB diffractometer with Cu Ka radiation. In Fig. 2a, the SEM image shows the graphene agglomerate, consisting of al- most transparent carbon nanosheets with thin wrinkled and silk-like structures. XRD patterns in Fig. 2b reveal that the graphene nanosheets' peak at 2h = 26.2°, which is the characteristic peak of graphene [38].
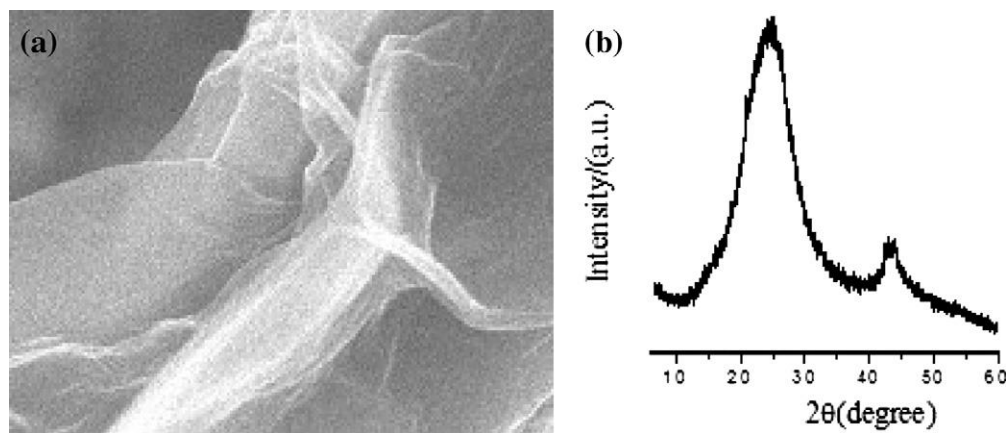

Figure 2.SEM image and XRD pattern.

2.4. Column preparation

Graphene (30.0 mg) was placed in a 3.0 mL SPE column using an upper frit and a lower frit to avoid adsorbent loss. Prior to extraction, the column was preconditioned with 10.0 mL meth-anol and 10.0 mL deionized water, respectively. The columnwas then   conditioned   to the desired   pH   with 5.0mL of 0.2 mol.L^{-1} acetate buffer solutions.

2.5. Recommended procedure

100.0 mL of the sample solution containing 100.0 µg L^{-1} of Mo was prepared. 2.5 mL of PAN (2.0 g L^{-1}) solution was added and the pH value was adjusted to 5.0 with acetate buffer solu-tion. The resulting sample solution was passed through the column at a flow rate of 2.0 mLmin^{-1}. After the solution passed through it completely, the column was rinsed with 5.0 mL ofdeionised water, and the analytes retained on the column wereeluted with 2.0 mL of 2.0 mol.L^{-1} HNO$_3$ in methanol at a flowrate of 2.0 mL min^{-1}. The analyte ions in the eluent weredetermined by FAAS. A blank was always taken through the whole procedure.

2.6. Sampling
Tap, sea, and riverwater samples usedfor the development of the method were collected in polytetrafluoroethylene (PTFE) containers from the Hebei Province. Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H_2O_2 and then concentratednitric acidwas added. These water samples were then filtered using a0.45 lm pore size membrane filter to remove suspended particulate matter and stored in a refrigerator in the dark before analysis.

3. Results and discussion
3.1. Effect of pH
Sample pH had a critical effect on the adsorption of target compounds by affecting the existing form of target   compounds, the charge species and density on the sorbents surface [39]. A series of experiments wasperformed byadjusting the pH from 2.0 to 10.0 with nitric acid, ammonium acetate, phosphate and ammonium chloride. The results illustrated in Fig. 3 reveals that the absorbance is nearly constant in the pH range of 5.0–7.0. The progressive decrease in the extraction ofMo at low pH is due to the competition of the hydrogen ion with the analyte for the reaction with PAN. Accordingly, pH 5.0 was selected for subsequent work and real sample analysis.

3.2. Influence of the amount of PAN
The effect of the amount of PAN on the absorption was studied using various volumes of the reagent ranging from 0.5 mL to 3.5 mL. The signal of Mo was increased with the increase of PAN volume up to 2.0 mL, and then kept constant. Hence,2.5 mL of 2.0 g L^{-1} PAN solution was chosen to account forother extractable speciesthat mightpotentially interfere with the assaying of Mo. volume, 2.5 mL; eluent type, 2.0 M HNO_3 in methanol; eluentvolume, 2.0 mL; concentration of Mo, 100.0 µg.L^{-1}sample and eluent solution, 2.0 mL min^{-1}
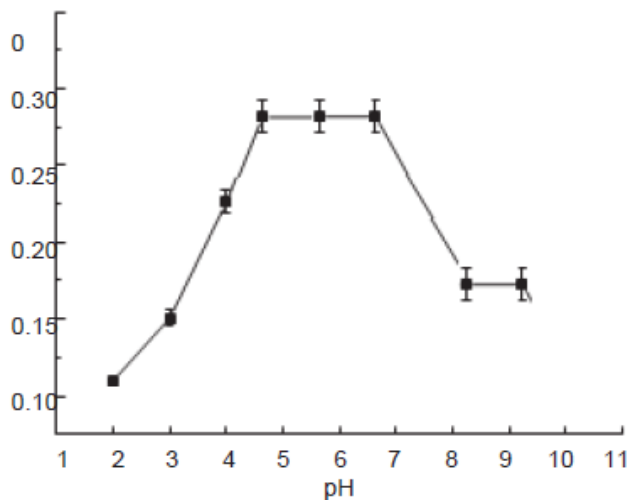
Figure 3. Effect of pH on the absorbance of Mo obtained from SPE- FAAS. Extraction conditions: water sample volume, 100.0 mL; PAN

3.3. Effect of flow rates of sample and eluent solution

The efficiency of metal preconcentration essentially depends on the flow rate of the sample solution to pass through themicro column, whereas the flow of eluent solutions affects the recoveries. The time taken is also a considerable factor. Therefore, the effect of the flow rate of the sample and eluent solutions on the recoveries of Mo on graphene was examined in the range of 0.5–5.0 mL min^{-1}. The flow rate of the sample and eluent solutions had no obvious influence on the quantitative recoveries of analytes at the range of 0.5–4.0 and 0.5–2.0 mL min^{-1}, respectively. A 2.0 mL min^{-1} flow rate of the sample and eluent solutions was chosen in subsequent experiments.

3.4. Breakthrough volume

The measurement of breakthrough volume is important in so- lid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without the loss of analyte during elution of the sample [40]. The breakthrough volume of the sample solution was tested by dissolving 10.0 µg of Mo in different volumes (25.0–1000.0 mL) and the recommended procedure was followed. It was observed that Mo was quantitatively recovered when the sample volume was less than 400.0 mL. When the sample volume exceeded 400.0 mL, the recoverywas decreased. The preconcentration factorfor preconcentration and extraction iscalculated by the ratio of the highest sample volume for analyte (400.0 mL) and the lowest final eluent volume (2.0 mL). In the present study the possible preconcentration factor was 200.

3.5. Adsorption capacity

In order to evaluate the adsorptive capacity of graphene, a batch method was used. 100.0 mL of solution containing
1.0 mg of metal ion at pH 5.0 was added to 30.0 mg sorbent. The mixture was filtered, after shaking for 10 min. 10.0 mL of the supernatant solution was determined by FAAS. The capacity of the sorbent forMo was found to be 20.6 mg g^{-1}.

Table 1. Effect of type and concentration of eluting agent on recovery of Mo.

Eluent	Recoverya (%)
1.0 M NaOH	63.6 ± 2.2
2.0 M NaOH	71.3 ± 2.6
1.0 M HCl	68.5 ± 2.3
2. M HCl	73.4 ± 2.4
3.0 M HCl	73.6 ± 2.3
1.0 M H$_2$SO$_4$	62.5 ± 2.4
2.0 M H$_2$SO$_4$	62.5 ± 2.1
0.5 M HNO$_3$	70.0 ± 2.2
1.0 M HNO$_3$	73.5 ± 2.3
2.0 M HNO$_3$	86.3 ± 2.3

0.5 M HNO_3 in methanol	85.4 ± 3.0
1.0 M HNO_3 in methanol	92.4 ± 3.0
2.0 M HNO_3 in methanol	94.8 ± 3.2

a Average of five determinations ± standard deviation.

3.6. Eluent type and its volume

In order to choose the best solvent for desorption of the ad- sorbed analytes on graphene, many reagent solutions were investigated. The results were given in Table 1. As can be seen, the recoveries of Mo were not so satisfactory when HCl, HNO_3, H_2SO_4 and NaOH were used as eluents solely. Good quantitative recovery for analyte ions could be obtained with 2.0 M HNO_3 in methanol. The effect of eluent volume on the recovery of Mo was also studied by using 2.0 M HNO_3 in methanol; it was found that quantitativerecoveries could be obtained with 2.0–4.0 mL of 2.0 MHNO_3 in methanol. Therefore, the volume of 2.0 mL of 2.0 mol $L-1$ HNO_3 in methanol was used in the following experiments.

3.7. Column reuse
To investigate the stability and the potential regeneration of the sorbent, several extraction and elution operation cycles were carried out following the column procedure. It was found that the column can be reused after being regenerated with 10.0 mL methanol and 10.0 mL double distilled water, and it is stable up to at least 50 adsorption–elution cycles without a significant decrease in the recovery of Mo. This is of great importance especially when the sorbent does the job with sat- isfactory analytical performance after using several circles in solid-phase extraction.

3.8. Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Mo on graphene were investigated. In these experiments, 100.0 mL solutions containing 100.0 µg L^{-1} of Mo and various amounts of interfering ions were treated according to the recommended procedure. The tolerance limit is defined as the ion concentra- tion causing a relative error smaller than ±5% related to the preconcentration and determination of analytes. The results, summarized in Table 2, show that the presence of major cations and anions in natural water has no significant influenceon the adsorption of Mo ion under the selected conditions.

Table 2.
Effect of interfering ions on the recovery of 100.0 µg L^{-1}Mo in water samples using SPE-FAAS.

Recovery of mercury (%)	Amount (µg)	Ions
98.4	100	Ca^{2+}
98.6	1000	
98.5	500	

98.6	100	Mg^{2+}
98.8	500	
98.8	1000	
98.4	5	Zn^{2+}
98.6	10	
98.7	25	
98.7	100	Cl^-
98.4	500	
98.4	1000	
98.6	100	NO_3^-
98.4	50	
98.3	1000	
98.7	100	SO_4^{2-}
98.2	500	
98.3	1000	
98.7	5	Co^{2+}
98.7	10	
98.7	25	
98.7	5	Cu^{2+}
98.3	10	
98.3	25	
98.7	100	Fe^{2+}
98.2	250	

3.9. Analytical performance

Under the optimized conditions, the calibration curve was obtained by preconcentrating a series of the solutions accord- ing to procedure under experiment. The curve was linear from5.0 to 240.0 µg L^{-1} for Mo. The calibration equation is $A = 3.16 \cdot 10-3C + 0.0042$ with a correlation coefficient of 0.9992, where A is the atomic absorbance of Mo, obtained by peak height, in the eluent at 240.5 nm and C is its concentra- tion in the sample solution (µg L^{-1}). The limits of detection and quantification defined as 3SB/m and 10SB/m (where SB is standard deviation of the blank and m is the slope of the cal- ibration graph) were 0.36 and 1.20 µg L^{-1}, respectively. The relative standard deviation (RSD) for ten replicate measure- ments of 20.0 and 100.0 µg L^{-1} of Mo were 3.45% and 3.18%, respectively.

3.10. Analytical application

The proposed method was used for the determination of Mo in several water samples. The results, along with the recovery for the spiked samples, are given in Table 3. The recoveries for the addition of different concentrations of Mo to water samples were in the range of 95.8–98.6%. To verify the accuracy of the proposed procedure, the method was used to determine of the content of Mo in the National Standard Reference Material for Environment Water (GSBZ 50030-94) after the appro- priate dilution. The results for this test are presented in Table 3. A good agreement between the determined values and the certified values was obtained.

Table 3 Analytical results of Mo determination (dissolved fraction) in certified reference materials and spiked natural water samples with the SPE-FAAS method (n = 3).

Recovery (%)	Sample volume (mL)	Mo (II) found (μg)	Mo(II) added (μg)	Sample
98.3	100	99.5	100	
98.6	250	99.5	100	Rain water[a]
97.9	1000	9.94	10	
98.5	100	9.95	10	
98.3	100	9.95	10	
98.2	200	9.95	10	
98.6	500	9.95	10	Snow water[b]
98.6	750	9.92	10	
98.5	1000	9.93	10	
95.8	100	13.65	-	GSBZ 50,030-94 (μg L-1)

[a] From rain water(Tehran, 20January, 2013)
[b]water (Tehran , 16 February ,2013)

3.11. Comparison with other sorbent materials

In this work, we report a comparison between graphene withseveral commonly used reserved-phase   sorbent   materialsincluding C_{18} silica, graphitic carbon, and CNTs. For this purpose, the same amount (30.0 mg) of different adsorbents was packed in 3.0 mL SPE columns. The columns were loaded with 100.0 mL of sample solutions containing 100.0 μg L^{-1} of Mo. All the work is done under the optimized conditions of graphene selected above. The C18 silica was evacuated from a Supelclean LC-18 SPE tube (Shanghai Chuding Instrument Company, Shanghai, China). The Ni in the flow-through, washing solution, and eluate were all determined.
As shown   in Table 4, the graphene-packed column   yields the highest recoveries (96.2%) among the studied adsorbents. This result definitely justifies the worth of graphene as an SPE adsorbent. Mo could be detected in the flow-through and washing solution after loading

on a C_{18} column, indicat- ing that 30.0 mg C_{18} silica is insufficient for the retention of chelates. To obtain acceptable results with C_{18}, more adsor- bent should be packed in the column to

Table 5 Comparison of some methods for preconcentration and determination of thal- lium with proposed method

enhance the adsorp- tion capacity. For instance, with a C_{18} column packed with 300.0 mg C_{18} silica, the recoveries of Mo can reach 93.5%. However, increasing the adsorbent amount will add to the cost of analysis and is unfavorable for instrument miniaturization. Graphitic carbon performed even more poorly than C_{18}. It was proposed that graphitic carbon did not give the expected extraction efficiency because of its large size and blank volume and less active sites for adsorption [41]. So it is noted that adsorption capacity of the adsorbents was generally in the following order: Graphene >C_{18} silica >Graphitic car- bon. For MWCNTs, the recovery was approximately 78.3%, which is evidently inferior to that of graphene. Recoveries for columns   using   SWCNTs   were   higher   than   MWCNTs, but still inferior to graphene. Increasing the volume of the eluent solvent can improve the recovery, e.g., with 5.0 mL HNO_3 as eluent solvent, the recovery of Mo on SWCNT   column can reach 92.3%. Nevertheless, increasing the volume of the eluent solvent will reduce the preconcentration factor.

Table 4. Comparison of the performance of graphene with several other adsorbents (C_{18} silica, graphitic carbon, SWCNTs, and MWCNTs) for the SPE of Mo.

Sorbent materials	Graphene	C18 silica	Graphitic carbon	MWCNTs	SWCNTs
Recoveries (%)	96.0	53.5	43.4	72.5	81.6

The advantage of graphene over C_{18} and graphitic carbon mainly lies in its higher sorption capacity. In addition, com- pared with CNTs, achieving complete elution with graphene is more facile. The above experimental results indicated that graphene   is a very promising adsorbent material.

3.12. Comparison with other solid phase adsorbents
The proposed methodology was compared to a variety of solid adsorbents reported recently in the literature. The distinct features are summarized in Table 5. As can be seen from the table, it is evident that the preconcentration factor obtained with alumina is comparable to or even better than most of the other chelating matrices. The other significant feature of the proposed method is the use of environmentally.

Reference	LDR (ng ml^{-1})	DL (ng ml^{-1})	Method
[42]	3.75–17.5	1	Solid–liquid extraction
[43]	0.1–100	0.08	Potentiometric
[44]	5–250	1	stripping
[45]	5–20	4	Liquid–liquid extraction
[46]	40–180.0	20	Microcrystalline naphthalene
–	5.0–240.0	0.36	Proposed method

4. conclusions

In conclusion, the proposed method reveals the great potential of graphene   as   an advantageous sorbent material in SPE. Using Mo as model analyte, the graphene-packed SPE columns showed reliable and attractive analytical performance in the analysis of environmental water   samples. Higher recoveries were achieved   with graphene   than   with other adsorbents including C_{18} silica, graphitic carbon, and CNTs, owing to the large surface area and unique chemical structure of graph- ene. Some other advantages of graphene as an SPE adsorbent have also been demonstrated, such as high sorption capacity, good reusability, and fine reproducibility. Although the ob- tained results of this research were related to the Mo determi- nation,   the   system   could   be   a   considerable   potential   guide for the preconcentration and determination of other metals.

Acknowledgements

References

1. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, D. *Sen, Chem. Rev.***1985,***85* ,271.

2. R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, *Chem. Rev*. **1991***,91*,1721.

3. R.M. Izatt, K. Pawlak, J.S. Bradshaw, R.L. Bruening, *Chem. Rev*. **1995**, *95* ,2529.

4. A.J. Blake, F. Demartin, F.A. Deviallonova, A. Garau, F. Isaia, V. Lippolis, M. Schroder, G. Verani, *J. Chem. Soc., Dalton Trans*. **1996**,3705.

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, *J. Chem. Soc., Dalton Trans*. **2001**, 1180.

6. V. Ghoulipour, S.W. Husain, *Acta Chromatographica*, **2002,***12***,** 170**.**

7. O. R .Hashemi,. M. Kargar-Razi,; F.Raoufi, A.Moghimi, H.Aghabozorg, M. R.Ganjali, *Microchem. J.*, **2001,**69,1.

8. N.I. Shcherbinina, G.V. Myasoedova, T.A. Khabazova, E.Y. Shroeva, G.R. Ishmiyarova, I.E. Nikitina, L.N. Bannykh, *Zh. Anal. Khim*. **1990**, *45* ,2137.

9. M.M. Gomes-Gomes, M.M. Hidalgo Garcia, M.A. Palacio Corvillo, *Analyst***1995***,120,*1911.

10. Unger K., *Porous Silica, Elsevier, Amsterdam*, 1979.

11. Boudreau S.P., Cooper W.T., *Anal. Chem*. 1989, **61** ,41.

12. Kvitek R.J., Evans J.F., Carr P.W., *Anal. Chim. Acta,*1982, **144** ,93.

13 .M.L. Bruening, D.M. Mitchell, J.S. Bradshaw, R.M. Izatt, R.L. Bruening, *Anal. Chem*. 1991, **63** , 21.

14. Mahmoud M.E., *Talanta* ,1997,**45** ,309.

15 . Mahmoud M.E., Soliman E.M., *Talata,*1997,**44**,15.

16 . Mahmoud M.E., Soliman E.M., *Talanta* ,1997,**44** ,1063.

17 Tong A., Akama Y., Tanaka S., *Anal. Chim. Acta* ,1990,**230** ,179.

18 . Dadler V., Lindoy L.F., Sallin D., Schlaepfer C.W., *Aust. J. Chem*. 1987, **40** ,1557.

19. A.MOGHIMI*,"Chinese Journal of Chemistry "***2007**,*25***,** 640.

20 . Mahmoud M.E., *Anal. Chim. Acta* ,1999,**398** , 297.

21 . Leyden D.E., Luttrell G.H., Sloan A.E., DeAngelis N.J*., Anal. Chim. Acta* ,1976,**84** ,97.

22 . Moghimi, A. Ghiasi R., Abedin A.R. , Ghammamy S. *African Journal of Pure and Applied Chemistry 2009,***3 (3),**pp. 051-059.

23 .Q.P. Liu, J.C. Liu, Y. Tong, J.K. Cheng, *Anal. Chim. Acta* 269 (1992) 223.

24 .Q.P. Liu, T. Zhao, J.C. Liu, J.K. Cheng, *Microchim. Acta* 122 (1996) 27.

25 .I.V. Mishenina, E.N. Shapovalova, T.A. Bolshova, P.V. Smirnov, O.A. Shpigun, *J. Anal. Chem.* 51 (1996) 270–276.

26 .H. Wang, H.S. Zhang, J.K. Cheng, *Talanta* 48 (1999) 1.

27 .H.Wang, H.S. Zhang, J.K. Cheng, P.H. Qiu *Microchem. J*. (1997) 332.

28. C.P. Zhang, D.Y. Qi, T.Z. Zhou, *Talanta* 29(1982) 1119.

29 .T.Z. Zhou, D.Y. Qi, C.P. Zhang, *Acta Chim. Sin*. 41(1983) 237.

30 . Zargaran M., Shoushtari A. M., Abdouss M*., J. Appl. Polym. Sci.* 2008, **110**, 3843.

31. Tabarzadi M., Abdouss M., Hasani S. A., Shoushtary A.M., *Mat.-wiss. u.Werkstofftech.***2010**, 41, No. 4,221

32 . Shin D. H., Ko Y. G., Choi U. S., Kim W. N., *Ind. Eng. Res*.2004, **43**, 2060.

33.P.Nayebi,; A.MOGHIMI, *Oriental Journal of Chemistry* 22(3) (2006) 507.

34.Mahmoud M.E., in: Proceeding of the 25th FACSS Conference, *Austin, TX, USA*, 11–15 October, 1998.

35. Wolf, S.F. ; Unger, D.L. ; Friedrich, J.M. *Anal. Chim. Acta* **2005**,*528* ,121.

36.Wang, Y.K., Gao, S.T., Zang, X.H., Li, J.C., Ma, J.J., 2012.*Analytica Chimica Acta* **716**, 112–118.

37.Narin, I., Soylak, M., 2003. *Talanta***60,** 215–221.

38.Rao, C.N.R., Biswas, Kanishka, Subrahmanyam, K.S., Govindaraj, A., 2009. *Journal of Materials Chemistry***19**, 2457–2469.

39.Jiao, Y.N., Ding, L., Fu, S.L., Zhu, S.H., Li, H., Wang, L.B., 2012. *Analytical Methods* **4**, 291–298.

40.Mester, Z., Sturgeon, R., 2003. Sample Preparation for Trace Element Analysis. *Elsevier*, Amsterdam.

41.Zhou, Q.X., Wang, W.D., Xiao, J.P., Wang, J.H., Liu, G.G., Shi, Q.Z., Guo, G.L., 2006. *Microchimica Acta***152**, 215–224.

42. Taher, M.A. ;*Bull. Korean Chem*. 2003,**24** ,1177.

43. Nascimento, P.C. ; Bohrer, D. ; Carvalho, L.M. ; Caon, C.E. ; Pilau, E. ; Vendrame, Z.B.; Stefanello, R. *Talanta* 2005,**65** ,954.
44. H. A. Becerril, J. Mao, Z. F. Liu, R. M. Stoltenberg, Z. N. Bao, Y. S. Chen, *ACS Nano* 2008, **2**, 463.
45. Z. F. Liu, Q. Liu, X. Y. Zhang, Y. Huang, Y. F. Ma, S. G. Yin, Y. S. Chen, *Adv.Mater*. 2008, **20**, 3924.
46. A.MOGHIMI,*Chinese Journal of Chemistry*2007,**2**5,10, 1536.
47. W. S. Hummers, Jr., R. E. Offeman*, J. Am. Chem. Soc.* 1958, **80**, 1339.