

Fabrication of NanoGraphene by new method Separation of Trace Amounts of Mo²⁺ in Water Samples Using

Ali Moghimi¹

¹ Department of Chemistry, Varamin(Pishva) Branch Islamic Azad University, Varamin, Iran
alimoghimi@iauvaramin.ac.ir

Abstract

A new sensitive and simple method was developed for the preconcentration 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 utilization 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 $\mu\text{g L}^{-1}$ with a detection limit of 0.36 $\mu\text{g L}^{-1}$. The relative standard deviation for ten replicate measurements of 20.0 and 100.0 $\mu\text{g L}^{-1}$ of Mo were 3.45 and 3.18%, respectively. Comparative studies showed that graphene is superior to other adsorbents including C₁₈ silica, graphitic carbon, and single- and multi-walled carbon nanotubes for the extraction of Mo. 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 appropriate performance 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 π -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 determination were systematically studied. The proposed method has been applied for the determination of 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

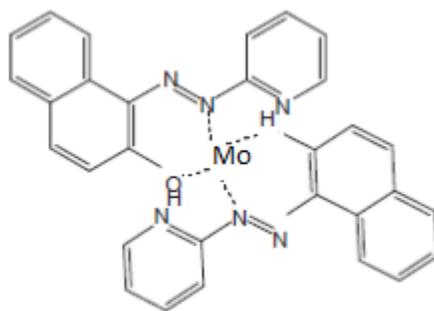


Figure 1. Structural formulae of the Mo-PAN complex.

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 were carried 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 $1000 \mu\text{g mL}^{-1}$ 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 prepared by dissolving the appropriate amount of PAN (Shanghai Chemistry 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 the 2–3 range, and ammonium acetate buffers (0.2 mol.L^{-1}) were prepared by adding an appropriate amount of acetic acid to ammonium 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 least 24 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 microscopy (SEM) using an S-3000N microscope and X-ray diffraction (XRD) measurement was carried out using a Rigaku D/max-rB diffractometer with Cu K α radiation. In Fig. 2a, the SEM image shows the graphene agglomerate, consisting of almost transparent carbon nanosheets with thin wrinkled and silk-like structures. XRD patterns in Fig. 2b reveal that the graphene nanosheets' peak at $2\theta = 26.2^\circ$, which is the characteristic peak of graphene [38].

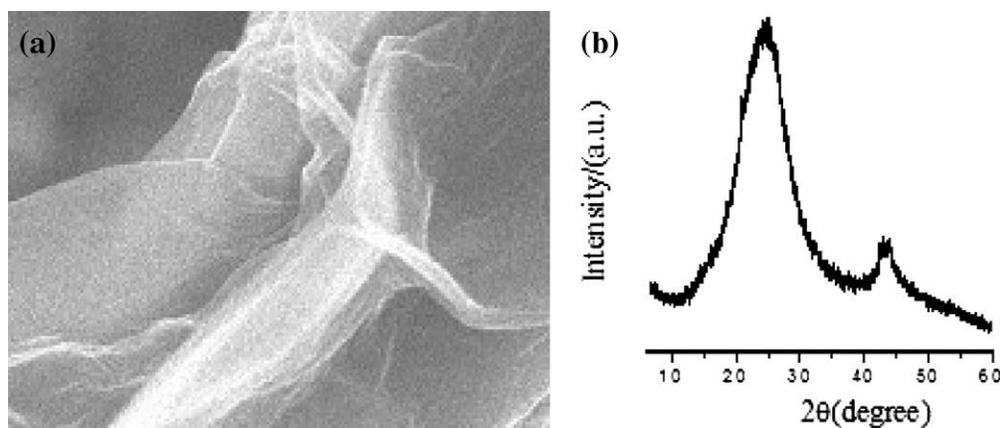


Figure 2. SEM image and XRD pattern.

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 methanol and 10.0 mL deionized water, respectively. The column was then conditioned to the desired pH with 5.0 mL of 0.2 mol.L $^{-1}$ acetate buffer solutions.

2.5. Recommended procedure

100.0 mL of the sample solution containing 100.0 $\mu\text{g L}^{-1}$ 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 solution. The resulting sample solution was passed through the column at a flow rate of 2.0 mL min $^{-1}$. After the solution passed through it completely, the column was rinsed with 5.0 mL of deionised water, and the analytes retained on the column were eluted with 2.0 mL of 2.0 mol.L $^{-1}$ HNO $_3$ in methanol at a flow rate of 2.0 mL min $^{-1}$. The analyte ions in the eluent were determined by FAAS. A blank was always taken through the whole procedure.

2.6. Sampling

Tap, sea, and riverwater samples used for 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% H₂O₂ and then concentrated nitric acid was added. These water samples were then filtered using a 0.45 μm 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 was performed by adjusting 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 of Mo 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 for other extractable species that might potentially interfere with the assaying of Mo. volume, 2.5 mL; eluent type, 2.0 M HNO₃ in methanol; eluent volume, 2.0 mL; concentration of Mo, 100.0 μg.L⁻¹ sample and eluent solution, 2.0 mL min⁻¹

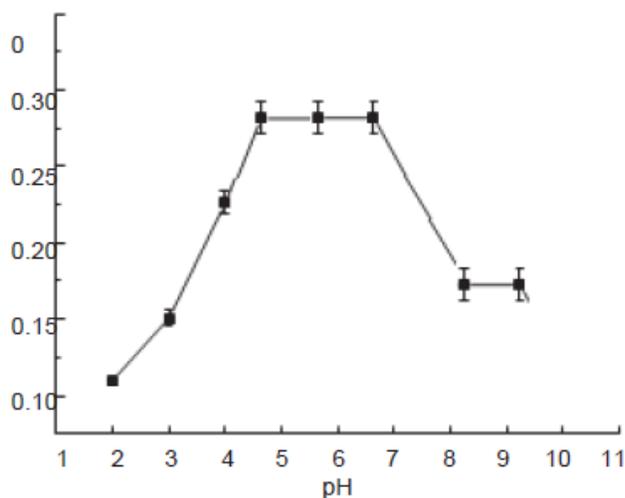


Figure 3. Effect of pH on the absorbance of Mo obtained from SPE- FAAS. Extraction conditions: water sample volume, 100.0 mL; PAN

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 the micro 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 solid 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 recovery was decreased. The preconcentration factor for preconcentration and extraction is calculated 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 for Mo was found to be 20.6 mg g⁻¹.

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

| Eluent | Recovery ^a (%) |
|--------------------------------------|---------------------------|
| 1.0 M NaOH | 63.6 ± 2.2 |
| 2.0 M NaOH | 71.3 ± 2.6 |
| 1.0 M HCl | 68.5 ± 2.3 |
| 2.0 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 adsorbed 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, HNO₃, H₂SO₄ and NaOH were used as eluents solely. Good quantitative recovery for analyte ions could be obtained with 2.0 M HNO₃ in methanol. The effect of eluent volume on the recovery of Mo was also studied by using 2.0 M HNO₃ in methanol; it was found that quantitative recoveries could be obtained with 2.0–4.0 mL of 2.0 M HNO₃ in methanol. Therefore, the volume of 2.0 mL of 2.0 mol L⁻¹ HNO₃ 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 satisfactory analytical performance after using several cycles 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 concentration 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 influence on 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 according to procedure under experiment. The curve was linear from 5.0 to 240.0 $\mu\text{g L}^{-1}$ for Mo. The calibration equation is $A = 3.16 \cdot 10^{-3}C + 0.0042$ 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 concentration in the sample solution ($\mu\text{g L}^{-1}$). The limits of detection and quantification defined as $3\text{SB}/m$ and $10\text{SB}/m$ (where SB is standard deviation of the blank and m is the slope of the calibration graph) were 0.36 and 1.20 $\mu\text{g L}^{-1}$, respectively. The relative standard deviation (RSD) for ten replicate measurements of 20.0 and 100.0 $\mu\text{g L}^{-1}$ 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 the content of Mo in the National Standard Reference Material for Environment Water (GSBZ 50030-94) after the appropriate 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 | Rain water ^a |
| 98.6 | 250 | 99.5 | 100 | |
| 97.9 | 1000 | 9.94 | 10 | |
| 98.5 | 100 | 9.95 | 10 | |
| 98.3 | 100 | 9.95 | 10 | Snow water ^b |
| 98.2 | 200 | 9.95 | 10 | |
| 98.6 | 500 | 9.95 | 10 | |
| 98.6 | 750 | 9.92 | 10 | |
| 98.5 | 1000 | 9.93 | 10 | |
| 95.8 | 100 | 13.65 | - | GSBZ 50,030-94 ($\mu\text{g L}^{-1}$) |

^a From rain water(Tehran, 20January, 2013)

^bwater (Tehran , 16 February ,2013)

3.11. Comparison with other sorbent materials

In this work, we report a comparison between graphene with several commonly used reserved-phase sorbent materials including C₁₈ 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 $\mu\text{g L}^{-1}$ 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 C₁₈ column, indicating that 30.0 mg C₁₈ silica is insufficient for the retention of chelates. To obtain acceptable results with C₁₈, more adsorbent should be packed in the column to enhance the adsorption capacity. For instance, with a C₁₈ column packed with 300.0 mg C₁₈ 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 C₁₈. 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 >C₁₈ silica >Graphitic carbon. 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.

Table 5 Comparison of some methods for preconcentration and determination of thallium with proposed method

| 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 |

Increasing the volume of the eluent solvent can improve the recovery, e.g., with 5.0 mL HNO₃ 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 (C₁₈ 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 C₁₈ and graphitic carbon mainly lies in its higher sorption capacity. In addition, compared 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.

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 C₁₈ silica, graphitic carbon, and CNTs, owing to the large surface area and unique chemical structure of graphene. 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 obtained 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

The authour wish to thank the Chemistery Department of Varamin(Pishva) branch Islamic Azad University for financial support.

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. Kvittek 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., *Talanta*, 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,**25**,10, 1536.
47. W. S. Hummers, Jr., R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.