

## Selective Solid Phase Extraction and Preconcentration of Ultra Trace Molybdenum Using Modified C<sub>18</sub> Membrane Disks

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A simple and reliable method for the selective extraction of ultra trace Mo(VI) ions using octadecyl-bonded silica membrane disks modified by  $\alpha$ -benzoinoxime and spectrophotometric determination with thiocyanate was developed. The influences of the sample matrix, amount of the extractant and type and minimum amount of the eluent and flow rates on the extraction efficiency were evaluated. Most of the cations examined have no interfering effect on the extraction and determination of molybdenum. However, effects of some interfering species such as Cu(II), Hg(II), Ce(IV) and Zr(IV) were decreased or eliminated in the presence of EDTA or rinsing of the membrane disk prior to the elution of the complex. The limit of detection of the proposed method is 0.08 ng/mL. The maximal capacity of the membrane disks modified with 40 mg of  $\alpha$ -benzoinoxime was found to be  $329 \pm 43$   $\mu$ g of molybdenum. The method was applied to the extraction and determination of molybdenum in natural waters, lucerne and spinach.

**Key Words:** Solid phase extraction,  $\alpha$ -Benzoinoxime, Molybdenum.

### INTRODUCTION

Molybdenum is an essential element for both animals and plants, having a major biological significance. It is also widely used in a variety of industrial processes, being an important constituent of metal alloys, pigments, lubricants and chemical catalysts, among others. Nevertheless, if present in more than low concentrations, it can be toxic<sup>1,2</sup>. Hence, the development of new methods for the selective separation and sensitive determination of molybdenum in ultra trace levels is still a challenging problem.

The determination of molybdenum is carried out by several analytical methods described in literature. These methods are based upon a wide range of analytical techniques such as spectrophotometry<sup>3,4</sup>, catalytic method<sup>5</sup>, polarography<sup>6</sup>, electron paramagnetic resonance spectrometry<sup>7</sup>, atomic absorption spectrometry<sup>8</sup> and inductively coupled plasma atomic emission spectrometry<sup>9,10</sup>. The thiocyanate spectrophotometric method is the most widely used method for this purpose, because of its simplicity, enough sensitivity and relatively low operation costs. Molybdenum forms an orange-red complex with thiocyanate ions in acidic media

in presence of reducing agents, that has an absorption maximum in the range of 460–470 nm<sup>11, 12</sup>.

Earlier, a number of extractants such as  $\alpha$ -benzoinoxime<sup>1</sup>, MIBK<sup>13</sup>, acetyl acetone<sup>14</sup>, LIX 622<sup>15</sup>, bis(2-ethylhexyl) phosphoric acid<sup>9</sup>, triphenylphosphine oxide<sup>16</sup>, diisododecylamine<sup>17</sup>, cupferron<sup>18</sup>, potassium ethylxanthate<sup>19</sup>, thiosulphate<sup>20</sup> and thiophosphinic acid<sup>21</sup> have been used for liquid-liquid extraction of molybdenum. However, the use of classical extraction methods for this purpose is usually time-consuming, labour-intensive and requires large amount of high purity solvents for extraction.

Solid phase extraction (SPE) or liquid-solid extraction is a popular and growing technique that is used for the sample preparation for analysis. It is an attractive alternative for the classical liquid-liquid extraction methods that reduces solvent usage and exposure, disposal costs and extraction time for sample preparation purposes<sup>22, 23</sup>. In recent years, the octadecyl-bonded silica SPE disks have been utilized for the extraction and separation of different organic compounds from environmental matrices<sup>24, 25</sup>. Moreover, the SPE disks modified by suitable ligands are successfully used for the selective extraction and concentration of metal ions<sup>26, 27</sup>. The aim of this work was the development of a rapid and efficient method for the selective extraction and concentration of ultra trace levels of Mo(VI) ion using the octadecyl silica membrane disks modified by  $\alpha$ -benzoinoxime (ABO) and its spectrophotometric determination with thiocyanate as a chromogenic reagent.

## EXPERIMENTAL

The absorbance measurements were carried out with a Shimadzu UV-160 spectrophotometer at 462 nm ( $\lambda_{\max}$ ). Extractions were performed with 47 mm diameter and 0.5 mm thickness Empore membrane disks containing octadecyl-bonded silica (8  $\mu$ m particles, 6 nm pore size, 3M Co., St. Paul, MN) with a standard Millipore 47 mm filtration apparatus connected to a vacuum pump. The typical composition of the disks was 90% (w/w) octadecyl-bonded silica and 10% (w/w) PTFE fibres. All acids were of the highest purity available from Merck and were used as received. Ethanol and DMSO were of HPLC grade from Merck. Reagent grade ammonium thiocyanate, stannous chloride, ferrous ammonium sulphate, ascorbic acid and ABO (all from Merck) were used as received. Analytical grade ammonium heptamolybdate tetrahydrate and other salts were of the highest purity available and were dried in a vacuum over P<sub>2</sub>O<sub>5</sub>. Doubly distilled deionized water was used throughout. Molybdenum stock solution (1000  $\mu$ g mL<sup>-1</sup>) was prepared by dissolving 1.5019 g of oven dried (300°C) MoO<sub>3</sub> in 20 mL of concentrated HCl, diluted to 1 L and stored. The molybdenum working solutions were prepared from the stock solution as needed.

In order to simplify the routine spectrophotometric determination of molybdenum with thiocyanate a cocktail solution was made. This solution was prepared as follows: 5.0 g of stannous chloride was dissolved in 10 mL of concentrated HCl in a 1000 mL volumetric flask. Then 0.6 g of ferrous ammonium sulphate, 50 g of ascorbic acid, 150 g of ammonium thiocyanate and enough distilled water

for the complete dissolution were added followed by dilution to the mark with water. This solution was directly added to the eluted complex from the disk for the spectrophotometric determination of molybdenum. The cocktail solution was stored in a refrigerator.

### Preparation of SPE membrane disks

In order to remove potential interferences and to ensure optimal extraction of the analyte of interest, the disk cleaning and conditioning should be done before its use<sup>26</sup>. Thus, after placing the membrane disk in the filtration apparatus, 10 mL of methanol was poured on to the disk and immediately drawn through the disk by applying a slight vacuum. After all of the solvent has passed through the disk, it was dried by passing air through it. The disk conditioning was then begun by pouring 10 mL of DMSO on to the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reached the surface of the disk. This is to ensure complete wetting of the disk with the organic solvent. Then, 10 mL of water was introduced on to the disk and was drawn through the disk. The disk was then dried under vacuum for 5 min or longer, if necessary. Then, a solution of 40 mg of ABO dissolved in 1 mL of DMSO was introduced on to the disk so that the solution was spread on the whole disk surface and was drawn slowly through the disk by applying a slight vacuum. The passed solution was collected in a proper test tube (25 × 200 mm). Then a few drops of water were added to the test tube (until just before appearance of a colloidal suspension) and the resulting mixture was again introduced to the reservoir and passed through the disk slowly. The filtration step was repeated until the passed solution was completely homogeneous and clear. Finally, the disk was washed with 10 mL of water and dried by passing air through it. The membrane disk modified by ABO is now ready for sample extraction. It should be noted that the modified disk thus prepared should be kept in a refrigerator for over a week, before its use for the extraction of molybdenyl ions.

### Solid phase extraction and quantification of Mo(VI)

After the conditioning, 50 mL of a 1.0 M HNO<sub>3</sub> solution containing Mo(VI) was passed through the membrane disk at 50 mL min<sup>-1</sup>. The disk was dried completely by passing air through it. A test tube 25 × 200 mm was then placed under the extraction funnel. The ABO-molybdenyl complex was eluted from the disk with ethanol (7 mL) at a flow rate of 7 mL min<sup>-1</sup>. Then the eluent was transferred into a 10 mL volumetric flask containing 2 mL of the cocktail solution and diluted to the mark with ethanol. The molybdenyl concentration was then determined at 462 nm against a reagent blank (external linear calibration range 0.5–5.0 µg/mL,  $r = 0.999$ ).

### General procedure for determination of Mo(VI) in real samples

(a) **Water samples:** Water samples were acidified and stored in a refrigerator using the PVC containers to the time when the determination possibility was brought about. Then, the filtrate was passed through an octadecyl silica membrane

disk without ABO to remove particles and organic compounds that may be present in the water. Enough concentrated  $\text{HNO}_3$  was added to achieve a concentration of 1.0 M and enough  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$  to reach a concentration of  $1.0 \times 10^{-3}$  M. The molybdenyl ions were extracted from the thus treated aliquot and then quantified as described above.

**(b) Spinach and Lucerne:** For the determination of molybdenum content of spinach and lucerne, 30.0 g of the well dried powder (mesh = 200) of each sample was transferred to a platinum crucible and ashed at 550–600°C for 3–4 h in a furnace. After cooling, the resulting ashes was transferred to a proper flask and was wetted with 12 mL of water followed by dissolution using 45 mL of 4.0 M HCl and dried at 60°C in a water bath. Then, 60 mL of 0.1 M  $\text{HNO}_3$  was added and the solution was filtered and diluted to 100 mL using 0.1 M  $\text{HNO}_3$  in a volumetric flask. Enough concentrated  $\text{HNO}_3$  and  $\text{Na}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$  was added to achieve concentrations of 1.0 M and  $1.0 \times 10^{-3}$  M, respectively. Finally, the recommended procedure for molybdenum determination was carried out.

## RESULTS AND DISCUSSION

Extraction of ABO-molybdenyl complex,  $(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N}_2)_2\cdot\text{MoO}_2$ , from acid medium is a selective method for separation of molybdenum<sup>13</sup>. Thus, some preliminary experiments were carried out in order to investigate the quantitative retention of molybdenyl ions by the octadecyl silica membrane disks in the absence and presence of ABO. It was found that the disk modified with 50 mg of the ligand is capable to quantitatively retain  $\text{MoO}_2^{2+}$  ions from 1.0 M  $\text{HNO}_3$  solution (10  $\mu\text{g}$  of molybdenum in 50 mL solution), while the bare membrane disks show no tendency to extraction of molybdenyl ions.

### Effect of the sample matrix and eluent

To investigate the influence of the matrix on the extraction of molybdenyl ions,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOH}$  and HCl solutions were tested. Solutions (50 mL) containing 10  $\mu\text{g}$  of molybdenum and varying concentrations of the acids were passed through the membrane disk modified with 40 mg of ABO. Molybdenyl ion is quantitatively extracted from 1.0–2.0 M  $\text{HNO}_3$  solutions (Fig. 1). Concentrations above 1.0 M of acid reduce the efficient lifetime of the disk. Thus, 1.0 M  $\text{HNO}_3$  was chosen as sample matrix. The observed decreasing of the recovery of molybdenum with increasing of HCl concentration is most probably due to the complex formation between molybdenyl and chloride ions at high concentrations of chloride<sup>14</sup>.

Organic solvents such as chloroform, methanol and ethanol were tested as eluent for the extracted ABO-molybdenyl complex from the disk. Ethanol was found to be the best eluent because it is a water miscible and proper solvent for cocktail solution components. Furthermore, ethanol accelerated the colour devel-

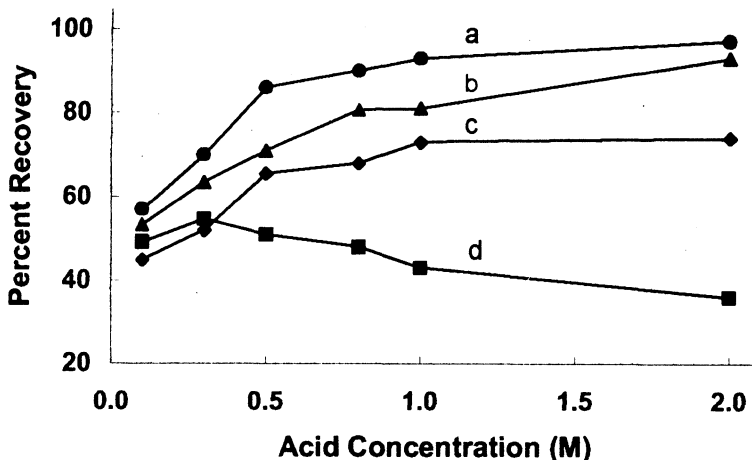


Fig. 1. Recovery of 10  $\mu\text{g}$  of molybdenum from 50 mL solutions containing different acids of varying concentrations by the membrane disk modified with 40 mg of ABO: (a) HNO<sub>3</sub>, (b) H<sub>2</sub>SO<sub>4</sub>, (c) CH<sub>3</sub>COOH, and (d) HCl.

opment<sup>1</sup>, with the least volume for elution and direct spectrophotometric determination of the ABO-molybdenyl complex.

#### Effect of amount of the ligand and flow rates

The optimal amount of ABO for the proper modification of the membrane disks was investigated (Fig. 2). The membrane disks modified with 35–60 mg ABO retain 10  $\mu\text{g}$  of molybdenum quantitatively. Thus, 40 mg of ABO was used for further studies.

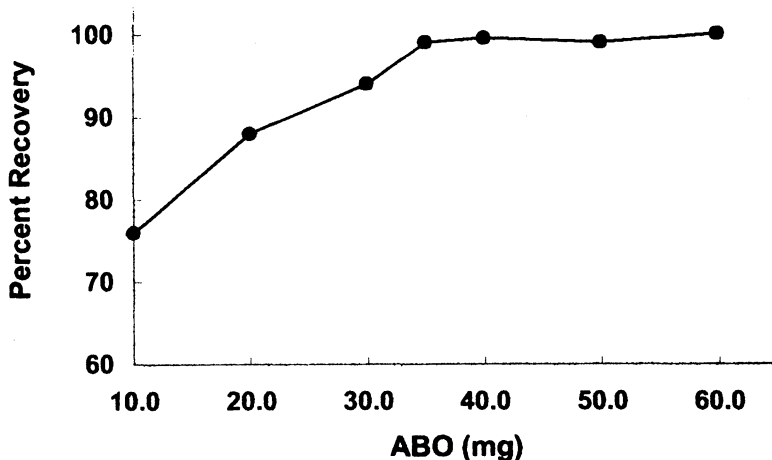


Fig. 2. Recovery of 10  $\mu\text{g}$  of molybdenum from 50 mL of 1.0 M HNO<sub>3</sub> solution by the membrane disk modified with varying amount of ABO.

The influence of the flow rates of the sample solution and ethanol through the membrane disks on the retention and recovery of molybdenyl ion was investigated. It was found that, in the range of 40–60 mL min<sup>-1</sup> the retention of molybdenum by the modified membrane disk is not affected by the sample flow rate significantly. It is interesting to note that, at the very low flow rates, the recovery of molybdenum decreases because of dissolution of the ligand in the sample solution. This fact was demonstrated by detection of ABO in the sample solution after passing it through the disk (at low flow rates). On the other hand, quantitative elution of ABO-molybdenyl complex from the disk was achieved in flow rates of 1–14 mL min<sup>-1</sup>. Thus, the optimum flow rates for the sample solution and eluent were chosen as 40 and 7 mL min<sup>-1</sup>, respectively.

### Analytical performance

When 10 µg of molybdenum in 10, 50, 100, 150, 200 and 250 mL sample solutions, under the optimal experimental conditions, were passed through the modified disks, the extraction was quantitative. Thus, the breakthrough volume for the proposed method should be greater than 250 mL. However, the solubility of the ligand in sample solution (especially at large volumes; long times of contacting the ligand and solution) strongly influences the breakthrough volume.

The maximal capacity of the membrane disk modified by 40 mg of ABO was determined by passing 50 mL portions of the sample solution containing 5000 µg of molybdenum, followed by the spectrophotometric determination of the retained molybdenum on the disk. The maximal capacity of the membrane disk obtained from the three replicate measurements was 329 ± 43 µg of molybdenum. The limit of detection (LOD) of the proposed method for the determination of molybdenum was studied under the optimal experimental conditions. The LOD obtained from  $C_{LOD} = k_b S_b / m^{28}$  for a numerical factor  $k_b = 3$ , is 0.08 ng/mL.

In order to investigate the selective separation and determination of molybdenyl ions from its binary mixtures with different metal ions, an aliquot of aqueous solutions (50 mL of 1.0 M HNO<sub>3</sub>) containing 10 µg molybdenum and different amounts of the other cations was taken and the recommended procedure was followed. The results are summarized in Table-1. The data given in Table-1 show that the membrane disks even in the presence of up to 15 mg of the other cations studied, retain the molybdenyl ions in the binary mixtures quantitatively. However, some of the species tried such as Cu(II), Hg(II), Ce(IV), Th(IV) and Zr(IV) interfere with the determination of molybdenyl ion. These interferences were eliminated or reduced considerably in the presence of EDTA, as a masking agent or by rinsing the disk with 50 mL of 1.0 M HNO<sub>3</sub> prior to the elution of the complex (Table-2).

TABLE-1  
SEPARATION OF MOLYBDENUM FROM THE BINARY MIXTURES<sup>a</sup>

Diverse ion	Amount taken ( $\mu\text{g}$ )	% Recovery of molybdenum	
Na <sup>+</sup>	13500	100.1	(3.2) <sup>b</sup>
K <sup>+</sup>	8300	98.2	(1.1)
Ca <sup>2+</sup>	9000	100.0	(3.8)
Mg <sup>2+</sup>	4100	102.0	(2.0)
Sr <sup>2+</sup>	200	101.0	(0.6)
Ba <sup>2+</sup>	15800	102.2	(2.5)
Fe <sup>3+</sup>	80	98.2	(1.3)
Cu <sup>2+</sup>	50	95.4	(4.5)
Co <sup>2+</sup>	35	97.3	(0.7)
Mn <sup>2+</sup>	350	96.1	(3.3)
Ag <sup>+</sup>	100	95.8	(5.3)
Pb <sup>2+</sup>	1300	100.3	(2.8)
Cd <sup>2+</sup>	3600	101.5	(1.2)
Hg <sup>2+</sup>	35	95.8	(4.6)
Al <sup>3+</sup>	60	97.5	(1.5)
Cr <sup>3+</sup>	250	97.8	(1.1)
Bi <sup>3+</sup>	100	102.5	(2.1)
Ce <sup>4+</sup>	1	97.3	(2.4)
Th <sup>4+</sup>	5	98.7	(2.5)
ZrO <sup>2+</sup>	10	102.9	(2.8)

<sup>a</sup> Initial samples contained 10  $\mu\text{g}$  of molybdenum and different amounts of the diverse cations in 50 mL of sample solution (1.0 M HNO<sub>3</sub>).

<sup>b</sup> Values in parentheses are % RSDs based on three replicate analyses.

To assess the applicability of the method to real samples, it was applied to the recovery and determination of added molybdenum from the three water samples. The results are summarized in Table-3. It is noteworthy that preliminary analyses using the proposed method did not show any molybdenum in these samples. The proposed method was also applied to determination of molybdenum in spinach and lucerne using the standard addition method. Satisfactory agreement exists between the results obtained by the proposed method and those reported by GF-AAS (Table-4).

TABLE-2  
 INFLUENCE OF EDTA AND RINSING<sup>a</sup> ON THE ERRORS PRODUCED BY  
 INTERFERING IONS IN THE RECOVERY OF MOLYBDENUM BY  
 THE MEMBRANE DISKS<sup>b</sup>

Interfering ion ( $\mu\text{g}$ )	Masking agent (M)	% Error
$\text{Fe}^{3+}$	(200)	—
	(200)	EDTA ( $1.0 \times 10^{-3}$ )
	(200)	Rinsing
	(100)	Rinsing
$\text{Cu}^{2+}$	(300)	—
	(300)	EDTA ( $1.0 \times 10^{-3}$ )
$\text{Hg}^{2+}$	(300)	—
	(300)	EDTA ( $1.0 \times 10^{-3}$ )
$\text{Ce}^{4+}$	(100)	—
	(100)	EDTA ( $5.0 \times 10^{-4}$ )
	(100)	EDTA ( $1.0 \times 10^{-3}$ )
	(100)	EDTA ( $1.0 \times 10^{-3}$ ) + Rinsing
$\text{Al}^{3+}$	(1000)	—
	(1000)	EDTA ( $1.0 \times 10^{-3}$ )
$\text{Th}^{4+}$	(100)	—
	(100)	EDTA ( $1.0 \times 10^{-3}$ )
	(100)	EDTA ( $1.0 \times 10^{-3}$ ) + Rinsing
$\text{ZrO}^{2+}$	(100)	—
	(100)	EDTA ( $1.0 \times 10^{-3}$ )

<sup>a</sup> Washing the disk with 50 mL 1.0 M  $\text{HNO}_3$  solution prior to the elution of the complex.

<sup>b</sup> Initial samples contained 10  $\mu\text{g}$  of molybdenum and different amounts of the diverse cations in 50 mL sample solution (1.0 M  $\text{HNO}_3$ ).

TABLE-3  
 RCOVERY OF 10  $\mu\text{g}$  MOLYBDENUM FROM DIFFERENT WATER SAMPLES<sup>a</sup>

Sample Site	% Recovery
Tap water (Khorram Abad, Jan 2003)	101.0 (3.3) <sup>b</sup>
Golastan Spring (Khorram Abad, Jan 2003)	99.1 (1.0)
Sarcheshmeh Spring (Khorram Abad, Jan 2003)	99.8 (1.8)

<sup>a</sup> 50 mL of each sample (EDTA =  $1.0 \times 10^{-3}$ ,  $\text{HNO}_3$  = 1.0 M) was taken.

<sup>b</sup> Values in parentheses are % RSDs based on three replicate analyses.



TABLE-4  
DETERMINATION OF MOLYBDENUM IN SPINACH AND LUCERNE

Sample	Molybdenum/Dry material ( $\mu\text{g/g}$ )			
	Proposed method		GF-AAS	
Spinach (Broojerd, April 2003)	14.8	(2.5) <sup>a</sup>	13.0	(0.3)
Lucerne (Broojerd, April 2003)	15.7	(1.1)	15.3	(1.8)

<sup>a</sup> Values in parentheses are % RSDs based on three replicate analyses.

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