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ORIGINAL PAPER

Determination of trace molybdenum in biological and water samples by graphite furnace atomic absorption spectrometry after separation and preconcentration on immobilized titanium dioxide nanoparticles

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Abstract A new method has been developed for the determination of trace molybdenum based on separation and preconcentration with TiO_2 nanoparticles immobilized on silica gel (immobilized TiO_2 nanoparticles) prior to its determination by graphite furnace atomic absorption spectrometry (GFAAS). The optimum experimental parameters for preconcentration of molybdenum, such as pH of the sample, sample flow rate and volume, eluent and interfering ions, have been investigated. Molybdenum can be quantitatively retained by immobilized TiO_2 nanoparticles at pH 1.0 and separated from the metal cations in the solution, then eluted completely with 0.5 mol L^{-1} NaOH. The detection limit of this method for Mo was 0.6 ng L^{-1} with an enrichment factor of 100, and the relative standard deviation (RSD) was 3.4% at the 10 ng mL^{-1} Mo level. The method has been applied to the determination of trace amounts of Mo in biological and water samples with satisfactory results.

Keywords Immobilized titanium dioxide nanoparticles · Preconcentration · Molybdenum · Graphite furnace atomic absorption spectrometry

Introduction

Molybdenum is one of the biologically essential microelements and has indispensable functions. Molybdenum requirement of adults amounts to about 25 μg each day [1]. Lack of molybdenum in the body may lead to diseases [2]. However, the over-ingestion of molybdenum will result in molybdenum poisoning. Some argue that the incidence of gout is related to excessive molybdenum. In addition, excessive molybdenum may disturb the metabolization of Ca and P, and cause osteoporosis and articular abnormity [3, 4]. Therefore, it is of great importance and significance for environmental science and life science to determine trace amount of molybdenum in water samples.

Graphite furnace atomic absorption spectrometry (GFAAS) is a very attractive option for the determination of trace amount of molybdenum in water samples. However, molybdenum in natural water exists in the form of MoO_4^{2-}, and the average concentration of molybdenum in sea and river water is about 10 and 1.5 μg L^{-1} [5], respectively, so that it cannot be determined directly by GFAAS, thus the preconcentration of molybdenum before its detection is needed. The most widely used techniques for separation and preconcentration of trace molybdenum include liquid–liquid extraction [6, 7], coprecipitation [8], solid-phase extraction [9–16], cloud point extraction [17] and liquid chromatography [18] etc. Recently, solid-phase extraction (SPE) technique has become increasingly popular in compared with the classical liquid–liquid extraction method because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents and the ability of combination with different detection techniques in the form of on-line or off-line mode [19]. Numerous substances have been applied as solid-phase extraction sorbents for preconcentration of molybdenum, such as chelating resin [9, 10], active carbon [11, 12], polyurethane foam [13], chitosan [14], microcrystalline triphenylmethane [15] and immobilized yeasts [16] etc.

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The field of nanocomposite materials has had the attention, imagination, and close scrutiny of scientists and engineers in recent years [20, 21]. Nanomaterials are made of nanoparticles; the regime of nanoparticle is from 1 nm to almost 100 nm, falls between the classic fields of chemistry and solid-state physics. One of the specific properties of nanomaterials is that a high percent of the atoms of the nanoparticle is on the surface. The surface atoms are unsaturated and can therefore bind with other atoms, possess highly chemical activity. Nanoparticulate metal oxides exhibit intrinsic surface reactivity and high surface areas, and can strongly chemisorb many substances, such acidic gases and polar organics [22]. Our previous studies show that nanometer TiO_2 material is a promising solid-phase extraction adsorbent for metal ions [23–26].

Due to the fine grain size of TiO_2 nanoparticles, when the suspension of TiO_2 nanoparticles is used for adsorption of metal ions, it is easy to coacervate and loss of activity, and difficult to be recovered. These problems can be avoided by immobilizing TiO_2 nanoparticles on different substrates. Immobilized TiO_2 nanoparticles can be prepared by coating the support substrates with a TiO_2 sol by different techniques such as chemical vapor deposition [27], chemical spray pyrolysis [28], and sol–gel method [29]. Among the different techniques, the sol–gel coating is the simplest, economical and has advantages such as TiO_2 is easily anchored on the substrates bearing the complicated shapes and large area substrates [30]. Immobilized TiO_2 nanoparticles have been widely applied as chemical sensors [31], electrochemical solar cells [32] and photocatalyst [33].

In this work, the adsorption behavior of molybdenum on immobilized TiO_2 nanoparticles was assessed. A new method using a microcolumn packed with immobilized TiO_2 nanoparticles as sorbent has been developed for the separation and preconcentration of molybdenum prior to its determination by GFAAS. Factors affecting the preconcentration of molybdenum, such as pH of the sample, sample flow rate and volume, eluent and interfering ions, were studied and optimized. The proposed method has been applied for the determination of trace molybdenum in biological and water samples.

Experimental

Apparatus

A TBS-990 atomic absorption spectrophotometer (Beijing Purkinge General Instrument Co. Ltd, Beijing, P. R. China) with a deuterium background correction and a GFH990 transversally heated graphite furnace atomizer system was used. A molybdenum hollow cathode lamp was employed as radiation source at 7.5 mA and 313.3 nm. All measurements were performed using integrated absorbance (peak area). The graphite furnace temperature program for the determination of Mo is given in Table 1. The pH values were measured with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. A HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, Shanghai, China) was used in separation/preconcentration process. A self-made PTFE microcolumn (20 mm×3.0 mm i.d.), packed with immobilized TiO_2 nanoparticles, was used in the manifold for separation/preconcentration. A minimum length of PTFE tubing with an i.d. of 0.5 mm was used for all connection.

Standard solution and reagents

Stock standard solution (1,000 μg mL^{-1}) of molybdenum was obtained from the National Institute of Standards (Beijing, P. R. China). Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Immobilized TiO_2 nanoparticles was prepared by sol–gel method in our laboratory as previously described elsewhere [34]. All reagents used were of the highest available purity and of at least analytical reagent grade. Doubly distilled water was used throughout.

Column preparation

Fifty milligrams of immobilized TiO_2 nanoparticles was introduced into a PTFE microcolumn (20 mm×3.0 mm i.d) plugged with a small portion of glass wool at both ends. Before use, 1.0 mol L^{-1} HCl solution and doubly distilled water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH with 0.1 mol L^{-1} NH_4Cl buffer solution.

General procedure

A portion of aqueous sample solution containing Mo was prepared, and the pH value was adjusted to the desired

Table 1 Operating parameters for GFAAS determination of Mo

Parameters	Values
Lamp current/mA	7.5
Wavelength/nm	313.3
Slit/nm	0.4
Ar flow rate/ mL min^{-1}	200 (stopped during atomizing)
Sample volume/μL	20
Temperature program	
Drying	100 °C (ramp 15 s, hold 15 s)
Ashing	1,000 °C (ramp 20 s, hold 15 s)
Atomizing	2,600 °C (ramp 0 s, hold 5 s)
Cleaning	2,700 °C (ramp 1 s, hold 3 s)

value with 0.1 mol L^{-1} HCl and 0.1 mol L^{-1} $NH_3 \cdot H_2O$. The solution was passed through the column by using a peristaltic pump adjusted to the desired flow rate. Afterwards, the retained Mo was eluted with 1.0 mL of 0.5 mol L^{-1} NaOH solution. The analyte in the eluent was determined by GFAAS. A blank was always taken through the whole procedure. The column could be used repeatedly after regeneration with 1.0 mol L^{-1} HCl solution and doubly distilled water respectively.

Sample preparation

Portions (0.5000 g) of standard reference materials (GBW07603 bush twigs and leaves and GBW07605 tea leaves, P. R. China) were transferred into PTFE beakers, 10 mL of concentrated HNO_3 and 3 mL of H_2O_2 were added, heated until the solution become transparent, continuously heated to near dryness and the residue dissolved in 0.1 mol L^{-1} HCl. After adjustment of pH to 1.0, the solution was made up to 100 mL with doubly distilled water.

Results and discussion

Effect of pH on adsorption

The pH value plays an important role with respect to the adsorption of different ions on oxide surfaces. According to Brunelle [35], the titania surface is positively charged when the pH of the solution is lower than the isoelectric point (IEP) of the oxide; whereas at pH above the IEP, the surface is negatively charged. Therefore, at pH below IEP, titania will adsorb anions; whereas at pH above IEP, cations will be adsorbed.

The effect of pH on the adsorption of Mo was studied at a concentration of 10 ng mL^{-1} of Mo and with a sample volume of 20 mL in the pH range of 0~5. The adsorption of Mo increases almost linearly from 70% at pH 0 to 100% at pH 1, and then almost linearly drops to 30% at pH 5. So a pH of 1.0 was selected as the compromise condition for the preconcentration of Mo. The metal cations are not adsorbed by immobilized TiO_2 nanoparticles in the pH range [34]. Thus, it is possible to preconcentrate of Mo and separate it from the metal cations.

Elution of the adsorbed Mo

It was found that the adsorption of Mo at pH >5 could be negligible. For this reason, NaOH solution at different concentrations was studied for the elution of retained Mo from the microcolumn at a flow rate of 0.5 mL min^{-1}. The recovery of Mo was calculated from the amount of Mo in the starting sample and the amount of Mo eluted from the column. It was found that the recovery of Mo is quantitative when NaOH concentration exceeds 0.3 mol L^{-1} whereas lower concentration gave only 60–80% recovery. To ensure complete elution, 0.5 mol L^{-1} NaOH is used as eluent in the following experiments.

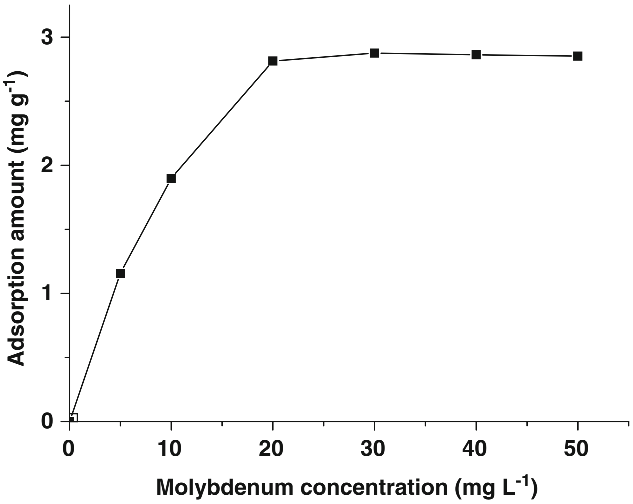

Fig. 1 Breakthrough curve of Mo on immobilized TiO_2 nanoparticles. pH: 1.0; sample volume: 25 mL

The effect of eluent volume on the recovery of Mo was also studied by keeping NaOH concentration of 0.5 mol L^{-1}, It was found that quantitative recovery of Mo could be obtained with 1.0 mL of 0.5 mol L^{-1} NaOH. Therefore, 1.0 mL eluent was used in the following experiments.

Effect of flow rate of sample solutions

The flow rate of sample solution affects the retention of Mo on the adsorbent and the duration of complete analysis. Therefore, the effect of the flow rate of sample solution was examined in a range of 0.5 to 2.5 mL min^{-1} under the optimum conditions (pH, eluent, etc.). It was found that the recovery of Mo was practically not changed up to a flow rate of 2.0 mL min^{-1}. The recovery of Mo decreases slightly when the flow rate is over 2.0 mL min^{-1} due to a decrease in the contact time between Mo and TiO_2 at higher

Table 2 Tolerance limits for coexisting ions in the adsorption of Mo

Coexisting	Tolerance limit of ions (mg L^{-1})
K^+	5,000
Ca^{2+}, Mg^{2+}	2,000
Cu^{2+}, Cd^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}	1,000
Cr^{3+}, Fe^{3+}, Al^{3+}	500
WO_4^{2-}, VO_4^{3-}	100
SiO_3^{2-}, SO_4^{2-}	1,000
PO_4^{3-}	200

Table 3 Comparison of the published methods with the proposed method in this work

Enrichment method	Detection method	Enrichment factor	Detection limit	Reference
LLE	Spectrophotometry	125	–	[7]
Coprecipitation	ETAAS	3.5	0.1 μg L^{-1}	[8]
SPE	ICP-AES	100	0.17 μg L^{-1}	[10]
SPE	ICP-AES	100	0.75 μg L^{-1}	[12]
SPE	GFAAS	10	0.08 μg L^{-1}	[13]
SPE	Spectrophotometry	83	0.013 μg L^{-1}	[15]
SPE	ICP-AES	480	0.021 μg L^{-1}	[16]
CPE	ICP-MS	70	0.8 ng L^{-1}	[17]
SPE	GFAAS	100	0.6 ng L^{-1}	This work

flow rate. Thus, a flow rate of 2.0 mL min^{-1} is employed in this work.

Effect of the sample volume

In order to explore the possibility of enriching low concentrations of analyte from large volume, the effect of sample volume on the retention of Mo ion was also investigated. For this purpose, 25, 50, 100, 150 and 200 mL of sample solutions containing 1.0 μg of Mo were passed through the microcolumn at optimum flow rate. It was found that quantitative recovery (>95%) was obtained for Mo up to a sample volume of 100 mL, the adsorbed Mo can be eluted with 1.0 mL 0.5 mol L^{-1} NaOH, so an enrichment factor of 100 could be achieved by this method.

Adsorption capacity

The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. The capacity study used was adapted from that recommended by Maquieira et al. [36], 25 mL aliquots of a series of concentrations (5~50 μg mL^{-1}) of Mo was adjusted to the appropriate pH, and the proposed procedure described above was applied. The amount of Mo adsorbed at each concentration level was determined. A breakthrough curve was obtained by plotting the concentration (mg L^{-1}) of Mo versus the milligrams of Mo adsorbed per gram TiO_2, and shown in Fig. 1. From the breakthrough curve, the adsorption capacity of immobilized TiO_2 nanoparticles for Mo was found to be 2.86 mg g^{-1}.

Table 4 Analytical results for molybdenum in standard reference materials (μg $g^{-1}\pm\sigma$, $n=3$)

Sample	Found	Certified value
GBW07603	0.29±0.04	0.28±0.03
GBW07605	0.035±0.004	0.038±0.006

Column reuse

The stability and potential regeneration of the column were investigated. The column can be reused after regenerated with 10 mL 1.0 mol L^{-1} HCl and 20 mL distilled water respectively, and stable up to at least 20 adsorption–elution cycles without obviously decrease in the recoveries for the studied ions.

Interferences

The effects of common coexisting ions on the adsorption of Mo on immobilized TiO_2 nanoparticles were investigated. In these experiments, solutions of 10 ng mL^{-1} of Mo containing the added interfering ions were treated according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Mo less than 90%, were given in Table 2. It can be seen that the presence of major cations and anions has no obvious influence on the adsorption of Mo ion under the selected conditions.

Table 5 Determination of Mo (ng mL^{-1}) in natural water samples ($n=5$)

Samples	Added	Found	Recovery (%)
Tap water	0	3.62±0.08	–
	5.0	8.38±0.16	95
	10.0	13.44±0.20	98
Lake water	0	4.54±0.10	–
	5.0	9.68±0.18	103
	10.0	14.36±0.22	98

Sample volume: 100 mL

Characteristics of the method

Under the optimum experimental conditions, the calibration curve for Mo was linear in the concentration range from 0.5 to 80 ng mL^{-1} with a correlation coefficient of 0.9974. The detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of seven replicate measurements of blank solution using the preconcentration method, was found to be 0.6 ng L^{-1} for Mo. The precision of this method (RSD), examined by 11 replicate measurements of 1.0 μg Mo in 100 mL of model solutions, was about 3.4%.

Table 3 compares the characteristic data of the present method with those reported in literatures. Generally, the enrichment factor obtained by the present method is comparable to those reported methods, and the detection limit is better than them. The higher enrichment factor reported in some references was obtained by using large volume of sample solution. On the other hand, the desorption step in our work is simple, because it works without heating or digesting, as necessary in some procedures [11, 12].

Analytical application

In order to establish the validity of the proposed procedure, the method has been applied to the determination of Mo in biological standard reference materials (GBW07603 bush twigs and leaves and GBW07605 tea leaves, P. R. China). The results are given in Table 4. As can be seen, the results obtained are in good agreement with reference values.

The proposed method was applied to the determination of Mo in tap water and lake water samples. Lake water sample was collected from East Lake, Wuhan, P. R. China, and tap water sample was freshly collected from our laboratory, after allowing the water to flow for 5 min. All water samples were filtered through a 0.45 μm membrane filter and analyzed as soon as possible after sampling. In addition, the recovery experiments of different amounts of Mo were carried out, and the results are shown in Table 5. The results indicated that the recoveries were reasonable for trace analysis, in a range of 95~103%.

Conclusion

It can be concluded from the results that immobilized TiO_2 nanoparticles is an effective sorbent for trace amounts of molybdenum and can be used for its preconcentration from the dilute aqueous solutions and separation from metal cations. The proposed method based on preconcentration with immobilized TiO_2 nanoparticles and determination by GFAAS showed enough sensitivity for trace molybdenum determinations in diverse kind of samples. The precision and accuracy were satisfactory. The method can be successfully applied to the separation, preconcentration and determination of molybdenum in real samples.

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