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Preconcentration and detection of ultra trace Molybdenum in Water, Biological, Food and Soft drinking Samples by Dispersive Liquid-Liquid Microextraction method

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Abstract

A sensitive method to determine the ultra-trace amounts of molybdenum is developed by dispersive liquid–liquid microextraction. This method is based on the reaction of molybdenum with thiocyanate in acidic media (HCl) and at present of ascorbic acid to form a red complex with the maximum absorption peak at 473 nm. In this method, the chloroform was used as an extractant solvent and cetyl trimethyl ammonium bromide (CTAB) was utilized as the disperser agent which also acts as the counter ion of Mo(V) anionic complexes. Under the optimum conditions, the calibration graph was linear over the range of 2.0-50.0 ng mL^{-1} of molybdenum with a detection limit of 0.6 ng mL^{-1}. The relative standard deviations (RSDs) for 5 and 30 ng mL^{-1} of molybdenum were 3.1 and 1.9 % (n=10), respectively. The proposed method was successfully applied to determine the molybdenum in the nail, water, wastewater, cereal, vegetable, fruit, and soft drinking samples.

Keywords: Cetyl trimethyl ammonium bromide (CTAB), Food samples, Microextraction, Molybdenum, Ultra-trace amount.

1. Introduction

Plants, animals, and humans need molybdenum for nitrogen, carbon, and sulfur metabolism. Molybdenum participates in a large number of enzymatic reactions [1]. It plays an important role in growth, healthiness, and the prevention of tooth decay. Molybdenum deficiency in humans is uncommon, but some clinical signs like tachycardia, headache, mental disturbances, and coma, have been observed in patients after prolonged total parenteral nutrition [2].

The fertilizers that contain molybdenum leads to increased agricultural productions. Therefore, molybdenum is very important in agriculture [3]. Molybdenum is used widely in industries such as the production of metal alloys, pigments, lubricants, and chemical catalysis.

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The determination of molybdenum is achieved by several techniques, such as flame and graphite furnace atomic absorption spectrometry (FAAS and GFAAS) [4-6], inductively coupled plasma mass spectroscopy (ICP-MS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], inductively coupled plasma — optical emission spectrometry with ultrasonic nebulization [9], electrochemistry [10], and spectrofluorimetry [11]. Most of these methods require specialized and relatively high-cost instruments. Therefore, its determination by the spectrophotometric method as a simple and low-cost method is an important advantage. Moreover, the concentration of molybdenum in environmental and industrial samples is very low, and matrix interferences are also serious. In order to overcome these problems, different preconcentration and separation methods have been employed, such as liquid–liquid extraction [12], ion exchange [13], solid-phase extraction [3], and cloud point extraction [2].

Dispersive liquid-liquid microextraction (DLLME) is one of the separations and preconcentration methods that firstly, was demonstrated by Rezaee et al. in 2006 [14]. In this method, a mixture of extraction and disperser solvents is injected into the aqueous sample and a cloudy solution is formed. Due to the large surface area of the interface between the two phases, the equilibrium state is achieved quickly, and therefore, the extraction time is very short. Some of its advantages are simplicity of operation, low consumption of solvents and samples, low cost, rapidity, high recovery, and high enrichment factor. Recently, this method has been applied for the preconcentration of trace organic and inorganic compounds in different samples [15, 16].

In this research, the DLLME method was applied to the preconcentration of Mo (VI) followed by micro-volume UV–vis spectrophotometric determination. Ascorbic acid reduces Mo(VI) to Mo(V) which is reacted with thiocyanate to form an orange-red complex. This compound is extracted into chloroform using the DLLME technique in the presence of CTAB as a disperser agent. This method has enough sensitivity and selectivity for the determination of Mo(VI) in various real samples.

2. Experimental procedure

2. 1 Chemicals and Reagents

All chemicals were of analytical grade. The Mo (VI) stock solution (1000 µg mL^{-1}) was prepared by dissolving 0.184 g of $(NH_4)_6Mo_7O_{24}$ (Merck, Germany) in water and diluting to 100 mL in a volumetric flask. More diluted solutions were prepared daily using this stock solution. A stock solution of 1 mol L^{-1} of thiocyanate was prepared by dissolving 9.72 g of the potassium thiocyanate (Merck, Germany) in water and diluting it to 100 mL in a volumetric flask. A 0.04 mol L^{-1} ascorbic acid (Merck, Germany) and 4 mol L^{-1} HCl (Merck, Germany) were prepared daily by dissolving appropriate amounts and diluting with water.

2. 2 Apparatus

A model Lambda-35 spectrophotometer (Perkin Elmer-USA) with 350 µL quartz microcells was used for absorbance measurements. To separate the phases, an ELE centrifuge (Kokusan-Japan) was used. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements were performed with a JY 2000 (HORIBA JOBIN YVON-France).

2. 3 General procedure

For DLLME under optimum conditions, 10 mL solutions containing 2.8×10-8–5.2×10-7 mol L^{-1} (2.0-50.0 ng mL^{-1}) of Mo(VI), 1.0×10-2 mol L^{-1} thiocyanate, 0.004 mol L^{-1} ascorbic acid, and 0.8 mol L^{-1} HCl were placed in a 10 mL glass tube with a conical bottom. Two hundred microliters of chloroform (extraction solvent) containing 0.003 mol L^{-1} CTAB were injected rapidly into the solution by using a microsyringe (ILS, Germany), and then the mixture was gently shaken. A cloudy solution was formed in the glass tube. The mixture was centrifuged for 5 min at 3500 rpm. Then sedimented chloroform was removed using a microsyringe and injected into the quartz microcell for analysis. The absorbance was measured at the wavelength of maximum absorbance 473 nm (against the blank). A blank solution

was also run under the same procedure without adding any molybdenum ion. The recovery was defined as the percentage of the total amount of analyte (m) that was extracted into the sedimented phase:

$R(\%) = (m_{sed} / m_0) \times 100 = (C_{sed} / C_0)\,(V_{sed} / V_{aq}) \times 100$

where V_{sed}, V_{aq}, C_{sed}, and C_0 are the volumes of the sedimented phase and the sample solution, concentration of the analyte in the sedimented phase, and initial concentration of the analyte in the aqueous sample, respectively. The C_{sed} was calculated from the analytical curve.

2. 4 Sampling

To analyze the beverage and nail samples, a wet digestion procedure was used. In the procedure, 3 mL of concentrated HNO_3 and 5 mL of 30 % (w/w) H_2O_2 were added to 30 mL of the beverage sample. Then, the samples were evaporated near dryness in order to remove excess H_2O_2 and to reduce the matrix effect and the analyte loss by volatilizing and diluting to 50 mL with 0.1 mol L^{-1} HNO_3 solution.

For the determination of the molybdenum content of tomato, peach, vetch, peas, bean, and rice, an adequate amount of wet samples were dried in an oven at 75 °C for 48 h. Determined weight of the well-dried powder of each sample was transferred to a porcelain crucible and laid in ashes at 500 °C for 8 h in a furnace. The residues were digested with nitric acid/hydrogen peroxide until complete dissolution of the sample was obtained. Finally, the recommended procedure for dispersive liquid-liquid microextraction and determination of molybdenum was carried out.

3. Results and discussion

Molybdenum (VI) reacts in acid media with thiocyanate ions and in the presence of a reducing agent to give an orange-red Mo(V)-thiocyanate complex ($[MoO(NCS)_5]^{2-}$) [3, 17]. The developed DLLME method is based on the extraction of this color product into chloroform. CTAB as a cationic surfactant played the role of disperser agent and also an ion-pairing reagent for the molybdenum (V) complex. In order to find the appropriate conditions for DLLME, different experimental parameters were studied and optimized.

3. 1 The effect of hydrochloric acid concentration

The reaction between molybdenum and thiocyanate occurs when the solution is acidified with a strong acid [17]. Therefore, the influence of hydrochloric acid concentration over the range of 0.08-1.60 mol L^{-1} on the dispersive liquid-liquid microextraction was studied. The results shown in Fig. 1 indicate that the absorption increased up to 0.80 mol L^{-1} of HCl and above this value, it decreased. Thus, 0.80 mol L^{-1} of HCl was selected as the optimum concentration.

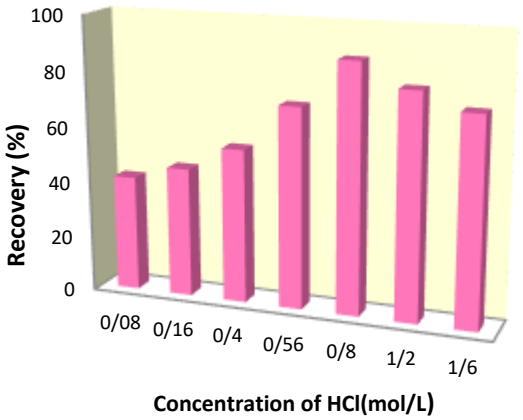

Fig. 1 Effect of HCl concentration on the determination of Mo.(DLLME conditions: Mo, 1.0×10^{-7} mol L^{-1}; sample volume, 10.0 mL; 4.0×10^{-3} mol L^{-1} `; 0.01 mol L^{-1} thiocyanate; injection 400 µL chloroform (extraction solvent) containing 0.005 mol L^{-1} CTAB (as disperser))

3. 2 The effect of thiocyanate concentration

The effect of SCN- concentration was studied in the range of 0.001 to 0.100 mol L^{-1}. The results are shown in Fig. 2. The absorption increased by increasing SCN^- concentration up to 0.01 mol L^{-1} and decreased gradually at higher ligand concentrations. Hence, 0.010 mol L^{-1} SCN^- was chosen as the optimal concentration. The cause of the decrease in absorbance at higher concentrations than 0.010 mol L^{-1} may be the reduction of ion-pairing reagent (CTAB); it means that SCN^- ions at high concentration formed ion pair with CTAB so the concentration of CTAB was not enough to form ion pair

with molybdenum (V) complexes.

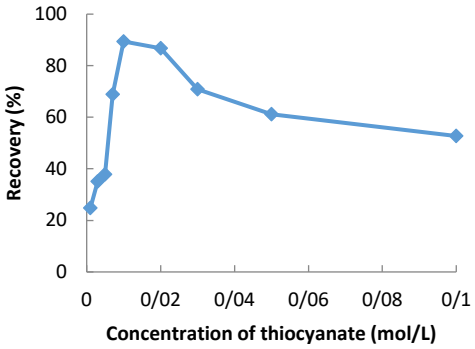

Fig. 2 Effect of thiocyanate concentration on the determination of Mo.(DLLME conditions: Mo, 1.0×10-7 mol L-1; sample volume, 10.0 mL; 0.8 molL−1 HCl; 4.0×10-3 mol L^{-1} Ascorbic acid; injection 400 µL chloroform (extraction solvent) containing 0.005 mol L^{-1} CTAB (as disperser))

3. 3 The effect of extraction solvent

The type of extraction solvent used in DLLME is an essential consideration for efficient extraction. It should be of higher density than water, high extraction capability of the interesting compounds, and low solubility in water. Chloroform ($CHCl_3$), dichloroethane ($C_2H_4Cl_2$), and carbon tetrachloride (CCl_4) were studied as extraction solvent using CTAB as the disperser. The results revealed that chloroform has the highest extraction efficiency and reproducibility in comparison with the other tested solvents. In addition, chloroform can form a stable cloudy solution and has less volume consumption. Therefore, chloroform was selected as an extraction solvent.

3. 4 The effect of CTAB concentration in extraction solvent

CTAB played two important roles: as disperser agent in extraction solvent and also as an ion-pairing reagent to form ion-pair with Mo (V) complexes because Mo (V) complexes are anion and CTAB is a cation. The influence of the CTAB concentration on the determination of Mo was evaluated in the concentration range of 0.001 to 0.010 mol L^{-1}, and the results are shown in Fig. 3. It can be seen that the absorbance increased with the increase of CTAB concentration up to 0.003 mol L^{-1}, and then remained constant. Thereby, CTAB concentration of 0.003 mol L^{-1} was selected for further study.

3. 5 The effect of injection solution volume

Since the preconcentration factor and sensitivity of the method is strongly dependent on the volume of the sediment phase, it was necessary to optimize the volume of the injection solution. In order to evaluate this parameter, different volumes of chloroform solution (150-400 µL) containing CTAB (0.003 mol L^{-1}) were examined with the same DLLME procedures. The results showed that the absorbance of the sedimented phase was increased with the increase of volume of chloroform from 100µL to 200µL, and then decreased when the volume of chloroform further increased. The increase of absorbance with increasing chloroform volume is due to dissolving more compounds in chloroform. But when the volume is over 200 µL, the preconcentration factor decreases by increasing the volume of chloroform be. Thus, 200 µL of chloroform was used throughout this study.

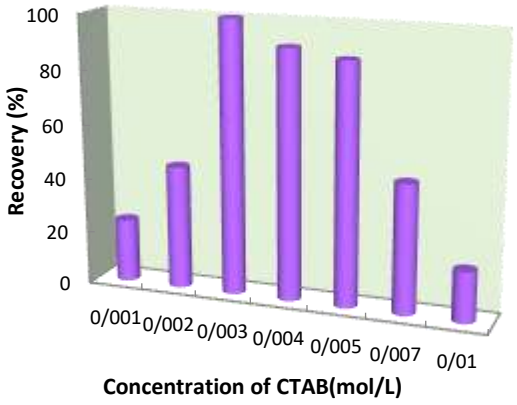

Fig. 3 Effect of CTAB concentration in extraction solvent. (DLLME conditions: Mo, 1.0×10-7 mol L^{-1}; sample volume, 10.0 mL; 0.8 mol L^{-1} HCl; 4.0×10^{-3} mol L^{-1} Ascorbic acid)

3. 6 The Effect of Time

The effect of extraction time (interval time between the injection of a mixture of dispersive solvent and extraction solvent, before starting to centrifuge) on the performance of DLLME is considered a key factor that must be studied and evaluated. Therefore, for evaluating this parameter, different extraction times (ranging from 0 to 30 min) with constant experimental conditions were studied. The maximum absorbance was achieved at lower than 30 s and above it had no significant effect on the absorbance of the organic phase. Therefore, an extraction time of 30 s was chosen for the subsequent experiments. According to the results, the extraction method is very rapid; this is

probably due to the large surface area between the extraction solvent and the aqueous phase. Therefore, this method is very fast and this is the most important advantage of DLLME technique.

Centrifugation is an important procedure for separating the extraction solvent from the aqueous solution in the proposed method, and centrifugation time could affect the volume of the sedimented phase. In order to attain the best extraction efficiency, the centrifugation time was optimized with a time span from 0.5 to 30 min at a rotation speed of 3500 rpm. A centrifugation time of 1 min was selected as the optimum since complete separation occurred during this time and no appreciable improvements were observed for a longer interval.

3. 7 Evaluation of method performance

After optimization of all parameters, quantitative characteristics of the proposed method were studied and the results are presented in Table 1. Linearity was observed over the range of 2.0–50.0 ng mL^{-1} with a correlation coefficient (r) of 0.9997. The limit of detection (LOD) (based $3S_b/m$) and limit of quantitation (LOQ) (based $10S_b/m$) of the method, were 0.6 and 2.1 ng mL^{-1} of molybdenum, respectively. The relative standard deviation for eight replicate measurements of 5 and 30 ng mL^{-1} of Mo(VI) were 3.1 and 1.9 %, respectively. The enrichment factor (EF) was defined as the ratio of the slopes of the regression lines, which is obtained by the proposed method and the direct measurement without preconcentration. The EF was found to be 57.

Table 1. Analytical performance data of DLLME method

Parameter	
Linear range (ng/mL)	2.0–50.0
Correlation coefficient	0.9997
Enrichment factor	57
LOD (3s, ng/mL; n=10)	0.6
LOQ (10s, ng/mL; n=10)	2.1
RSD for 5 ng mL^{-1} of Mo (%, n=10)	3.1
RSD for 30 ng mL^{-1} of Mo (%, n=10)	1.9

3. 8 Interference Studies

In order to evaluate the selectivity of the method, the effects of different ions on the determination of molybdenum were investigated. A constant concentration of molybdenum (1.0×10^{-7} mol L^{-1}) was taken with different concentrations of ions and the general procedure was followed. Any deviation of ±5% or more from the absorbance value of the standard solution was considered interference. Results given in Table 2 indicate that the proposed method is relatively selective for the determination of molybdenum.

Table 2. Tolerance limit of foreign ions on determination of Mo(VI).

Interference	Intinterference/Ag Ratio
Co^{2+},Ba^{2+}, $Cr_2O_7^{2-}$, Na^+, Cd^{2+}, Ag^+, K^+, CO_3^{2-}, Mg^{2+}, Pb^{2+}, Cr^{3+}, SO_4^{2-}, Ni^{2+}, NO_3^-, Ca^{2+}, Al^{3+}, Mn^{2+}, F^-, Pd^{2+}	1000
Cl^-	200
CH_3COO^-	100

3. 9 Analysis of real samples

The proposed procedure was applied to the determination of trace molybdenum in different real samples. Mineral, tap, and river water and also wastewater samples were collected from the khouzestan (in Iran) and analyzed by DLLME as a prior step to its enhanced spectrophotometric determination. No concentration of molybdenum in the water and wastewater samples was detected. Each type of water was spiked with variable amounts of Mo(VI) to assess matrix effects. The results are shown in Table 3 and the relative recoveries of molybdenum from mentioned water samples at various spiking levels were between 95.0 and 102.0 %. In addition, we decided to analyze nail, food, and beverage samples by the proposed method and validate it by recovery of appropriate amounts of Mo(VI) standard solution to the sample. The results of these determinations and the recoveries for the spiked samples are listed in Table 4. As shown in Table 4, in all cases, the extraction efficiency of molybdenum and recoveries was excellent and showed no serious matrix effects. Also, to evaluate the applicability of the method, the results of

samples were compared with those obtained by using inductively coupled plasma atomic emission spectrometry (ICP–OES). The results of paired t-test showed no significant difference at 95% confidence level.

Table 3. Determination of molybdenum in water samples.

sample	Added Mo (ng/mL)	Founded[a] Mo (ng/mL)	Recovery (%)
Tap water1	0	N.D[b]	-
	10	10.0 ± 0.1	100.0
	20	20.1 ± 0.2	100.5
Tap water2	0	N.D	-
	10	9.9 ± 0.1	99.0
	20	20.0 ± 0.2	100.0
River water	0	ND	-
	10	9.5 ± 0.1	95.0
	20	19.1 ± 0.1	95.5
Mineral water	0	ND	-
	10	9.9 ± 0.1	99.0
	20	20.1 ± 0.1	100.5
wastewater	0	ND	-
	10	10.2 ± 0.1	102.0
	20	19.9 ± 0.2	99.5

a: Mean ± standard deviation(n=4), b: Not Detected

Table 4. Determination of molybdenum in food and beverage samples.

Sample	Added (ng/mL)	Found[a] (ng/mL)	Recovery (%)	ICP/OES (ng/mL)	t-test[b]	F-test[c]
Nail	-	18.12±0.15	-	17.91±0.03	2.38	25
	10	27.93±0.22	98.1			
	20	39.07±0.35	104.7			
Tomato	-	4.97±0.06	-	5.02±0.02	1.36	9
	10	14.78±0.25	98.5			
	20	25.01±0.34	100.4			
Rice	-	7.38±0.08	-	7.49±0.02	2.32	16
	10	17.37±0.16	99.9			
	20	26.57±0.28	95.9			
Peach	-	9.40±0.09	-	9.36±0.02	0.75	20
	10	19.88±0.13	104.8			
	20	28.64±0.23	96.2			
Whole green beans	-	19.68±0.16	-	19.78±0.03	1.06	28
	10	29.85±0.21	101.7			
	20	40.21±0.29	102.6			
Whole white beans	-	N.D	-	0.09±0.01	-	-
	10	9.81±0.11	98.1			
	20	20.98±0.24	104.9			
Peach juice	-	11.61±0.10	-	11.57±0.02	0.68	25
	10	22.01±0.17	103.0			
	20	31.62±0.26	99.6			
Orange juice	-	2.97±0.08	-	3.06±0.02	1.90	16
	10	12.52±0.15	95.5			
	20	23.27±0.23	101.5			
Apple juice	-	6.76±0.09	-	6.65±0.02	2.07	20
	10	16.43±0.24	96.7			
	20	26.64±0.32	99.4			

a Mean ± standard deviation (n = 3).

b Tabulated t-value for four degrees of freedom at 95% confidence level is 2.78.

c Tabulated F-value for (2, 2) degrees of freedom at 95% confidence level is 39.

Table 5. Comparison of the proposed method with some of the previously reported methods for the determination of Molybdenum by spectrophotometric method.

Methods/Reagents used	Linear range (ng/mL)	LOD (ng/mL)	Real sample	Ref
Cloud-point Extraction	7.5-1800	2.18	Beverages and food sample	2
Solid Phase Extraction	Up to 5000	38	Soil and plant	3
Cloud point extraction	7.9–160	2.3	water and milk	18
Cloud point extraction	160–1800	50	water and plant	19
DLLME	8–192	2.4	tap water and multivitamin	20
salicylaldehyde-benzoylhydrazone	$10\text{-}6\times10^{4}$	1	biological, food and vegetables	21
Secondry ligand extraction method	0.9×10^{-6}-1.1×10^{-5}M	-	Dental alloy wiron99	22
Direct determination	0-600	6.6	Plant tissues	23
Homogeneous liquid–liquid extraction	500-5000	-	Biological and Environmental sample	24
Cloud point Extraction	-	0.8	plant	25
Atomic Absorbtion spectrometry	110-5100	-	nail	26
Cloud-point Extraction	0.3-320.0	0.1	Tap water, well water and steel	27
spectrophotometry	6.2 – 50.0	0.88	river waters	28
Catalytic spectrophotometric	0.1-4.0	0.04	Different water and waste water	29
DLLME	5.0-100.0	1.43	Water and plant	30
A non-extraction sequential injection	40-1920	21	Drinking water and mineral water	31
Liquid Liquid Extraction	1200-2600	2.39	Spinach and lucerne sample	32
DLLME	2.0-50.0	0.2	Biological, soft drinking, cereal, food, different water samples	Present work

3.10. Comparison of the method with other published methods

A comparison between the analytical performances of our system with previously reported methods for the determination of Mo is presented in Table 5. As shown, the proposed method has a wide linear range and a more favorable detection limit than other compared methods [2, 3, 18-26, 28, 30-32], with the exception of two method [27, 29]. This method has been used successfully to detect Mo in different types of real samples and is unique in the variety of the real samples in comparison with all the methods in Table 5.

4. Conclusion

The simple, fast, sensitive, efficient, inexpensive, high accuracy and precision method for determination of trace amount of Mo (VI) in the difference samples was developed by combining the DLLME technique with spectrophotometric detection method. The goal of this combination was because of spectrophotometric method advantages of rapidity, simplicity, cost effectiveness, and availability of instrument. Ascorbic acid reduces Mo(VI) to Mo(V) which is reacted with thiocyanate to form an orange-red complex. This compound is extracted into chloroform using the DLLME technique in the presence of CTAB as a disperser agent. Some characteristics of previously reported methods such as limit of detection and linearity were summarized in Table 5 for the comparison. As it can be seen, the suggested preconcentration method in this work showed an appropriate linearity in comparison to the previous methods and had relative low limit of detection for the preconcentration of Mo (VI). Finally, the proposed method was successfully applied for determination of Mo (VI) in different real samples.

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