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Homogeneous liquid–liquid extraction method for the selective separation and preconcentration of ultra trace molybdenum

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Abstract

A new simple and efficient homogeneous liquid–liquid extraction method for the selective separation and preconcentration of molybdenyl ions was developed. α-Benzoin oxime (ABO) was investigated as a complexing ligand, and perfluorooctanoate ion ($PFOA^-$) was applied as a phase-separator agent under strongly acidic conditions. Under the optimal conditions ($[ABO] = 2.1 \times 10^{-3}$ M, $[PFOA^-] = 1.8 \times 10^{-2}$ M, $[HNO_3] = 1.7$ M, [acetone] = 11.8% (v/v)), 10 μg of molybdenum in 5 ml aqueous phase could be extracted quantitatively into 40 μl of the sedimented phase. The maximum concentration factor was 125-fold. Thiocyanate was applied as a chromogenic reagent for the direct spectrophotometric determination of molybdenum in the sedimented phase. The reproducibility of the proposed method is at the most 2.4%.

The influence of the type and concentration of acid solution, the concentration of ABO, the type and volume of the water-miscible organic solvent, the concentration of $PFOA^-$, and the effect of different diverse ions on the extraction and determination of molybdenum(VI) were investigated. The proposed method was applied to the extraction and determination of molybdenum(VI) in natural water, Spinach, and Lucerne samples. A satisfactory agreement exists between the results obtained by the proposed method and those reported by GF-AAS.

Keywords: Homogeneous liquid–liquid extraction; Molybdenum; α-Benzoin oxime

1. Introduction

Molybdenum is an essential element for both animals and plants and is the only metal of the second transition series, which is of 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 catalysis, among others. Nevertheless, if present in more than low concentrations it can be toxic [1,2]. Hence, the development of new methods for the selective separation and sensitive determination of molybdenum in ultra trace levels is still a challenging problem.

Homogeneous liquid–liquid extraction is a simple and powerful preconcentration method that reduces the extraction time, disposal costs, consumption and exposure to the organic solvents. This method extracts the solute in a homogeneous solution into the very small sedimented phase formed from the solution by the phase-separation phenomenon. The ternary component solvent system and the perfluorinated surfactant system are the two usual modes of homogeneous liquid–liquid extraction. In homogeneous liquid–liquid extraction, the initial condition is homogeneous solution, namely, there is no interface between the water phase and the water-miscible organic solvent phase. In other words, the surface area of the interface is infinitely large initially. Accordingly, no vigorous mechanical shaking is necessary. The procedure is simple and requires only the addition of the reagent [3]. Recently, homogeneous liquid–liquid extraction was successfully utilized for the extraction of some organic

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and inorganic analytes [4–15]. We now report of a simple and efficient method for the selective extraction and preconcentration of molybdenyl ions using homogeneous liquid–liquid extraction with α-benzoin oxime (ABO) as a complexing ligand, perfluorooctanoate ion ($PFOA^-$) as a phase-separator agent and the spectrophotometric determination of $MO_2{}^{2+}$ with thiocyanate [16,17] as a chromogenic reagent.

2. Experimental

2.1. Reagents and solutions

All acids were of the highest purity available from Merck and were used as received. Ethanol, methanol, acetone, acetonitrile, THF and DMSO were of HPLC-grade from Fluka or Merck. The reagent-grade perfluorooctanoic acid (HPFOA), ammonium thiocyanate, stannous chloride, ferrous ammonium sulphate, ascorbic acid and ABO (all from Merck) were used as received. The analytical-grade molybdenum(VI) oxide and other salts were of the highest purity available and were dried in a vacuum over P_2O_5. Doubly distilled deionized water was used throughout. A perfluorooctanoate standard solution (0.1 M) was prepared by neutralizing HPFOA with 0.1 M LiOH and diluted with the same solution for use. The molybdenum(VI) stock solution (1000 $\mu g\,ml^{-1}$) was prepared by dissolving 1.5019 g of oven dried (300 °C) MoO_3 in 20 ml of 12.0 M HCl, diluted to 1000 ml and stored. The molybdenum(VI) working solutions were prepared from the stock as needed.

In order to simplify the routine spectrophotometric determination of molybdenum with thiocyanate, a *cocktail solution* was made [1]. This solution was prepared as follows: 5.0 g of stannous chloride was dissolved in 10 ml concentrated of 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 complete dissolution was added followed by dilution to the mark with water. This solution was stored in a refrigerator. Both stannous chloride and ascorbic acid were used as reducing agents for the Mo(VI)–SCN reaction. The cocktail solution has been directly added to the sedimented phase for the spectrophotometric determination of molybdenum(VI).

2.2. Apparatus

Absorbance measurements were carried out with a Shimadzu UV-1650PC double-beam spectrophotometer and a 1 ml quartz cell at 462 nm (λ_{max}). A Shimadzu AA6650 atomic absorption spectrometer equipped with a GFA-EX7 graphite furnace (with high-density graphite tube cuvettes), an ASC-6100 autosampler, and a D_2 continuous source for background correction, was utilized for the testing of real samples. An Eppendorf 5810 centrifuge was used for centrifugation.

2.3. Homogeneous liquid–liquid extraction and quantification of molybdenum(VI)

A sample solution (5 ml) containing 10 μg of molybdenum was placed in a 50 ml cylindrical glass vial fitted with a plastic cap, 1 ml of acetone containing 4 mg of ABO and 1.5 ml of a 0.1 M $PFOA^-$ solution were added. The mixture was allowed to stand for 5 min at room temperature, and then centrifuged for 10 min at 2000 rpm after addition of 1 ml of concentrated HNO_3. The final concentrations were $[ABO] = 2.1 \times 10^{-3}$ M, $[PFOA^-] = 1.8 \times 10^{-2}$ M, $[HNO_3] = 1.7$ M, and [acetone] = 11.8% (v/v). The sedimented phase (40 μl) was removed using a 100 μl micro-syringe and transferred into a spectrophotometer cell containing 200 μl of the cocktail solution and diluted to 1 ml with ethanol. The molybdenyl concentration was then determined at 462 nm against a reagent blank (external linear calibration range, 0.5–5.0 $\mu g\,ml^{-1}$; $r = 0.998$).

2.4. Determination of molybdenum(VI) in natural water samples

A 50 ml aliquot of the water sample was first passed through a 45 μm (Millipore) nylon filter to remove any particles that may have been present in the natural water samples. The molybdenyl ions were extracted from the 5 ml portion of the thus-treated aliquot using the proposed method and then quantified as described in the previous section.

2.5. Determination of molybdenum(VI) in Spinach and Lucerne samples

For determination of the 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 laid in ashes at 550–600 °C for 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 HNO_3 was added and the solution was filtered and diluted to 100 ml using 0.1 M HNO_3 in a volumetric flask. Finally, the recommended procedure for homogeneous liquid–liquid extraction and determination of molybdenum was carried out. To access the accuracy of the results they were tested using GF-AAS. The optimum parameters of GF-AAS experiments were as follow: wavelength: 313.3 nm; lamp mode: BGC-D_2; drying: 250 °C, 20 s; ashing: 1000 °C, 23 s; atomization: 2600 °C, 3 s.

3. Results and discussion

Molybdenum is an amphoteric element with predominantly acidic properties. Molybdenum occurs principally in the +VI oxidation state as molybdate ($MoO_4{}^{2-}$) ions, which form condensed species in an acid media. In strongly acidic solutions, molybdenyl cations (MoO_2^{2+}) occur. Extraction of the ABO–molybdenyl complex, $(C_{14}H_{12}O_2N_2)_2 \cdot MoO_2$, from the acid medium is a selective method for the separation of molybdenum [1,18,19]. Thus, we examined ABO for the homogeneous liquid–liquid extraction of molybdenum. Preliminary experiments showed that molybdenyl ions were sufficiently extracted from an acidic solution in a system containing acetone and $PFOA^-$ as a phase-separator agent. The proposed method was investigated as a preconcentration method for the spectrophotometric determination of molybdenum using thiocyanate.

3.1. Effect of the type and concentration of acid solution

To investigate the influence of the matrix on the homogeneous liquid–liquid extraction of molybdenyl ions, different concentrations of HNO_3, HCl and H_2SO_4 were tested. A colloidal suspension was formed instead of the formation of an oily drop, using H_2SO_4 solution. HCl solution gave a high viscose drop, which was not suitable for the up-take into a micro-syringe. However, 1.7 M HNO_3 gives an extraction percent of 92.0. Thus, different concentrations of HNO_3 were tested for the homogeneous liquid–liquid extraction of molybdenum. The results (Fig. 1) show that the concentrations greater than 1.7 M cause a decrease in the extraction percent of molybdenum, due to the protonation of donating atoms (O and N) in the ABO structure. This protonation of donating atoms inhibits the formation of Mo-ABO complex. Because of the incomplete phase-separation, no drop was formed using concentrations less than 1.5 M. Hence, 1.7 M HNO_3 was used for further studies.

3.2. Effect of the concentration of ABO

The effect of the concentrations of ABO on the extraction percent of molybdenum is shown in Fig. 2. The results show that the extraction percent of molybdenum increases with increasing the concentration of ABO, but in very high concentrations, the phase-separation occurs precociously, before the extraction is completed and solid sediment is remained. Thus, concentration of 2.1×10^{-3} M of ABO was used for further studies.

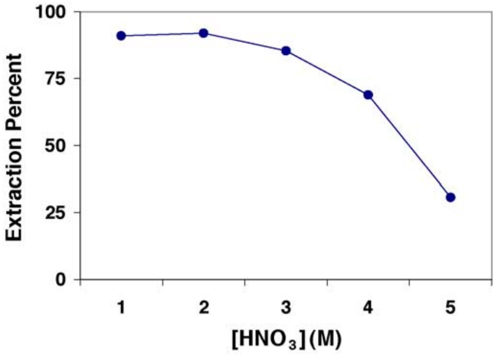

Fig. 1. The effect of HNO_3 concentration on the percent extraction of molybdenum using ABO (10 μg of molybdenum in 5 ml of HNO_3 solution).

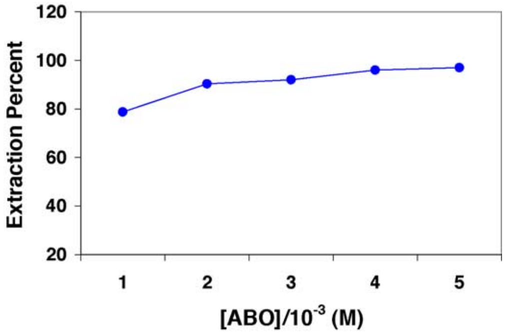

Fig. 2. The effect of ABO concentration on the percent extraction of molybdenum (10 μg of molybdenum in 5 ml of 1.7 M HNO_3 solution).

3.3. Effect of the nature and volume of the water-miscible organic solvent

Different organic solvents such as THF, DMSO, acetone, ethanol, methanol and acetonitrile were tested for the homogeneous liquid–liquid extraction of molybdenyl ions using ABO (Table 1). The results show that in the presence of acetone, the highest extraction percent for molybdenyl ions is achieved in addition to the formation of a proper oily drop. On the other hand, its application causes a complete phase-separation with the least amount of the solvent resulting in a viscose spherical drop suitable for handling with a micro-syringe. Thus, acetone was selected for subsequent experiments. Furthermore, the volume of acetone was optimized. The results show that the extraction percent of molybdenum increases with increasing the volume percent of acetone. The use of very large volumes causes a delayed phase-separation and a poor reproducibility of the extraction percent data due to disturbing the spectrophotometric measurements. Hence, an 11.8 vol.% of acetone was used as the optimal volume for the homogeneous liquid–liquid extraction of molybdenyl ion using ABO.

3.4. Effect of the $PFOA^-$ concentration

In order to investigate the optimum amount of $PFOA^-$ on the quantitative homogeneous liquid–liquid extraction

Table 1
Effect of water-miscible organic solvent on the extraction percent of molybdenyl ions and volume of sedimented phase[a]

Organic solvent	Volume of sedimented phase (μl)	Extraction (%)
THF	25	–[b]
DMSO	25	9.3
Ethanol	28	65.0
Methanol	32	17.0
Acetone	40	92.0
Acetonitrile	50	15.3

[a] Ten micrograms of molybdenum in 5 ml of 1.7 M HNO_3 solution, $[ABO] = 2.1 \times 10^{-3}$ M.

[b] It indicated a very high unreliable absorbance and poor reproducibility.

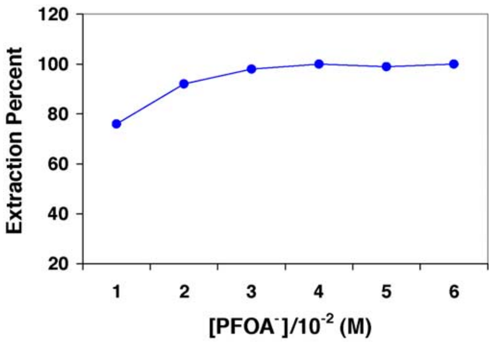

Fig. 3. The effect of $PFOA^-$ concentration on the percent extraction of molybdenyl ions (10 μg of molybdenum in 5 ml of 1.7 M HNO_3 solution, $[ABO] = 2.1 \times 10^{-3}$ M).

of molybdenyl ions using ABO, the extraction of 10 μg of molybdenum from 5 ml of the sample solutions under the optimal experimental conditions was conducted by varying the concentration of $PFOA^-$ (Fig. 3). As seen, the extraction of molybdenyl ions is quantitative above 1.7×10^{-2} M of $PFOA^-$. Hence, subsequent homogeneous liquid–liquid extraction experiments were carried out with 1.8×10^{-2} M of $PFOA^-$. Although the reproducibility of the results increases with decreasing $PFOA^-$ concentration, the extraction percent of molybdenum decreases too. The poor reproducibility of the results with high concentrations of $PFOA^-$ is related to affecting its surfactant properties on the spectrophotometric measurements due to the micelle formation in the solution.

3.5. *Analytical performance*

When 10 μg of molybdenum in 5, 10, 20, 30, 40 and 50 ml of solutions were examined under the optimal experimental condition ($[ABO] = 2.1 \times 10^{-3}$ M, $[PFOA^-] = 1.8 \times 10^{-2}$ M, $[HNO_3] = 1.7$ M, and [acetone] = 11.8% (v/v)) using the proposed method, the molybdenum(VI) was quantitatively extracted in all cases. This matter shows that the volume of the sample solution does not affect the extraction percent because in any volume the concentrations of HNO_3, ABO and $PFOA^-$ are constant and it is just enough to centrifuge the sample solution correctly using a suitable vessel. A high sample solution volume causes a high sedimented phase volume. It is a point that was not taken into account in the similar previous studies [4–10]. Hence, the concentration factor is limited to the ratio of the sample and the sedimented phase volumes. Thus the maximum concentration factor of the proposed method was 125-fold (i.e., 40 μl of the sedimented phase was produced from 5 ml of the sample solution).

In order to investigate the selective extraction and determination of molybdenyl ions using ABO from binary mixtures with various metal ions, an aliquot of a solution (5 ml) containing 10 μg of molybdenum and different amounts of other cations were taken and the recommended procedure was followed. The results (Table 2) show that the molybdenyl ions in the binary mixtures were extracted almost completely even in the presence of up to 4 mg of some cations. However, some of the species tried such as WO_4^{2-} interfere with the determination of molybdenyl ions. The reproducibility of the proposed method for the homogeneous liquid–liquid extraction and determination of 10 μg of molybdenum from 5 ml of the sample solution was also studied. The results obtained on the 10 replicate measurements revealed an R.S.D. of 2.4%.

Table 2
Separation of molybdenum(VI) from binary mixtures using ABO[a]

Diverse ion	Amount taken (μg)	Recovery of molybdenum (%)
Na^+	4000	99.5
K^+	4000	98.6
Ba^{2+}	4000	101.2
Ca^{2+}	3500	99.5
Mg^{2+}	3000	100.1
Sr^{2+}	1000	99.8
Pb^{2+}	800	102.1
Mn^{2+}	400	101.9
Cr^{3+}	200	101.6
Cd^{2+}	200	103.1
Cu^{2+}	100	99.5
Co^{2+}	100	97.7
Ag^+	100	98.6
Al^{3+}	100	99.8
Fe^{3+}	100	100.1
Hg^{2+}	50	98.9
VO^{3-}	30	97.5
WO_4^{2-}	5	95.3

[a] Ten micrograms of molybdenum in 5 ml of 1.7 M HNO_3 solution, $[ABO] = 2.1 \times 10^{-3}$ M, $[PFOA^-] = 1.8 \times 10^{-2}$ M, [acetone] = 11.8% (v/v).

To evaluate the applicability of the proposed method to samples with different matrices, it was applied to the separation and recovery of molybdenyl ions from three different natural water samples (Table 3). The results show that, in all samples, the molybdenum recovery is almost quantitative. The proposed method was also applied for the determination of molybdenum in Spinach and Lucerne collected from different sites in the Lorestan Province. A satisfactory agreement exists between the results obtained by the proposed method and those reported by GF-AAS (Table 4). The results of the proposed method for the analysis of molybdenum in Spinach and Lucerne were compared with the results

Table 3
Recovery of 10 μg molybdenum from different natural water samples in Khorram-Abad city (December 2003)[a]

Sample site	Recovery (%)
Well water (Dareh-Garm)	99.8 (1.1)[b]
Tap water (Lorestan University)	98.7 (1.5)
Golastan Spring water (Falak-al-Aflak Castle)	99.5 (2.5)

[a] Five millilitres of each sample solution ($[ABO] = 2.1 \times 10^{-3}$ M, $[PFOA^-] = 1.8 \times 10^{-2}$ M, $[HNO_3] = 1.7$ M, [acetone] = 11.8% (v/v)) was taken.

[b] Values in the parentheses are %R.S.D.s. based on three replicate analyses.

Table 4
Determination of molybdenum in Spinach and Lucerne samples collected from different sites in Lorestan Province (February 2003)[a]

Sample site	Molybdenum/dry material ($\mu g\ g^{-1}$)	
	Proposed method	GF-AAS
Lucerne (Khorram-Abad city)	10.5 (1.4)[a]	7.3 (2.9)
Lucerne (Boroojerd city)	15.8 (1.7)	15.2 (3.8)
Spinach (Boroojerd city)	13.5 (2.0)	13.0 (1.4)
Spinach (Pole-Dokhtar city)	11.3 (1.7)	10.8 (2.2)

[a] Values in the parentheses are %R.S.D.s. based on three replicate analyses.

of GF-AAS method using *F*-test. This test shows that there is not any statistically difference between the precise of the two methods in the uncertainty level of 5%.

4. Conclusion

Homogeneous liquid–liquid extraction utilizes a phase-separation phenomenon from the homogenous solution and makes it possible to rapidly and powerfully concentrate analytes. The proposed HLLE method is simple, selective and sensitive. The proposed procedure can be successfully applied to separation, preconcentration and determination of molybdenum in different real samples.

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