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Application of Microfunnel Magnetic Stirring Assisted Liquid-Liquid Micro-extraction Method for Pre-concentration and Determination of Silver Ion in Water Samples

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Abstract

In this research, a highly sensitive, selective, rapid and simple micro-funnel magnetic stirring-assisted liquid–liquid microextraction (MF-MSA-LLME) method combined with flame atomic absorption spectrometry (FAAS) was introduced for the preconcentration, extraction, and measurement of trace amounts of silver ion. In this method 1-(2–Pyridylazo)-2-naphthol (PAN) and 1-octanol were used as chelating agent and extraction solvent. Effective parameters on extraction efficiency such as pH of sample solution, type and volume of extraction solvent, amount of ligand, extraction time, and ion strength were investigated and optimized. Under the optimum conditions, calibration curve was linear in the range of 2-250 μg L^{-1} with correlation of coefficient r^2=0.997. Detection limit, relative standard deviation and the enrichment factor were 0.251 μg L^{-1}, 4% (n=7, C=80 μg L^{-1}) and 135, respectively. The proposed procedure was successfully applied for the preconcentration and determination of trace amount of silver in water samples with good accuracy and good validity.

***Keywords**: Micro-funnel magnetic stirring, Assisted liquid–liquid microextraction, Silver, Flame atomic absorption spectrometry, Water samples.*

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Introduction

Metal ions play a serious role in various fields of science and technology.Silver, as a precious metal is applied in accessories, tableware, mirrors, coins, photographic materials, cosmetics and ornament [1]. Recently, silver inputs into natural water resources have been increased due to the use of silver and silver-containing compounds in several applications and everyday used products [2-5]. It is well known that silver and silver compounds are highly toxic to many biological systems [6, 7]. Thereby, the development of analytical methods for the determination of trace amounts of silver is important in many fields. Due to the low concentration of silver in environmental samples and the matrix effects, the direct determination of silver at trace amounts is usually difficult. So, the usage of sensitive and selective techniques, such as flame atomic absorption spectroscopy (FAAS) [8], electrothermal atomic absorption spectrometry (ETAAS) [9-11], inductively coupled plasma optical emission spectrometry (OCP-AES) [12], and spectrophotometric techniques [13,14], combined with a novel separation preparation, is very necessary. Several techniques have been used for the separation and pre-concentration of silver, such as co-precipitation [15], liquid-liquid extraction (LLE) [16], solid-phase extraction (SPE) [17] and cloud point extraction (CPE) [18]. But some disadvantages of these methods are: being time-consuming, unsatisfactory enrichment factors, usage of large organic solvents and secondary wastes, limitation in their applications. So, several novel micro-extraction methods have been developed to overcome these problems. Dispersive liquid–liquid micro-extraction (DLLME), as a new mode of liquid phase micro-extraction (LPME) method, was introduced in 2006 by Assadi and coworkers [19,20]. DLLME has many advantages such as high enrichment factor, simplicity, rapidity, short extraction time, ease of operation, low cost, and low consumption of organic solvents. However, one of the serious drawbacks of DLLME is its limited choices of extraction solvent. Therefore, in recent years, some researchers made great effort to use low-density solvents micro-extraction methods and different extraction devices [21-26]. In the most mentioned methods, collecting a thin layer of extractant floating on the top of the aqueous sample is usually difficult. In this regard, bell-shaped extraction device assisted liquid–liquid micro-extraction (BSED–LLME); based on using a low density organic solvent was introduced by Radomir Cabala et al [27]. In our previous work, we introduced micro-funnel magnetic stirring-assisted dispersive liquid–liquid micro-extraction technique for determination of 3-chloro-4-(dichloromethyl)-5-hydroxy-2 (5H)-furanone in aqueous samples by GC-ECD [28].

This study describes a new, simple and cheap micro-extraction technique, based on the use of a modified micro-funnel device for extraction and determination of silver in water samples, combined with flame atomic absorption spectroscopy (FAAS). A homemade micro-funnel vessel is used to introduce a simple and rapid way to collect hydrophobic species from aqueous solutions. Extraction process was performed without the use of disperser solvent and centrifugation step. After extraction, the organic phase was moved to the capillary tube of micro-funnel by injecting a few milliliter of distilled water into the vial through the rubber cap, which holds the micro-funnel to the glass tube. Experimental parameters, which may affect the extraction performance, were studied and optimized.

Experimental

Reagent and chemicals

Reagent grade 1-undecanol, 1-dodecanol, 1-decanol and n-octanol, were purchased from Merck (Darmstadt, Germany) as extraction solvent. Analytical grade Ag (I) nitrate and nitrate salts of other cations (all from Merck, Darmstadt, Germany) were available with high purity and used without further purification. Working solutions of Ag (I) were prepared daily by diluting a 1000 mg L^{-1} stock solution. All solutions were prepared using doubly distilled water. 1-(2- Pyridylazo)-2-naphthol (PAN) (Merck, Darmstadt, Germany) as chelating agent was prepared by dissolving an appropriate amount of reagent in n-octanol. The pH of Ag solutions was adjusted with the aid of nitric acid and sodium hydroxide. The glassware was kept in a 5% (v/v) nitric acid solution overnight and subsequently washed with doubly distilled water.

Apparatus

The flame atomic absorption spectrophotometer (Shimadzu AA-680, Japan) equipped with deuterium background correction was used for measurement of silver. A silver hollow cathode lamp (Hamamatsu, Photonic Co. Ltd, L233-series) was employed as the radiation source at a wavelength of 328.1 nm and acetylene flow rate of 1.8 L min^{-1}. A pH meter (Metrohm Lab-827, Switzerland) was used for adjustment of the pH of sample solution. Stirring the sample solution was carried out by Magnetic stirrer (IKA RH basic 2, Germany). A homemade micro-funnel vessel was applied for extraction process.

General procedure

According to Figure 1a, 50 mL solution containing 80 µg L^{-1} of Ag(I) and $NaNO_3$ (0.1% w/v) was adjusted to pH=12. Next, the prepared solution was transferred into a cylindrical glass vial (13 cm height and 28 mm i.d.) and 200 µL of PAN solution (300µg in n-octanol) was lightly injected on the sample solution surface by a 250 µL Hamilton syringe. The cap of the micro funnel was placed on the cylindrical vial, the solution was firmly stirred at 1200 rpm for 2 minute and a cloudy solution was formed, due to the dispersion of many fine droplets of n-octanol (Figure 1b). Afterwards, the magnetic stirrer was stopped and separation of the two phases took place in one minute (Figure 1c). Accordingly, the organic phase was collected on the top of the solution (Figure 1d). Next, a few milliliters of doubly distilled water were injected into the vial through the rubber cap, which holds the micro-funnel to the glass tube. . The organic phase was moved into the capillary tube of micro-funnel (Figure 1e), was manually withdrawn using a 250 µL syringe, poured into the eppendorf vial, diluted to 300 µL by methanol (Figure 1f)and was injected to the flame atomic absorption spectrometer for analysis.

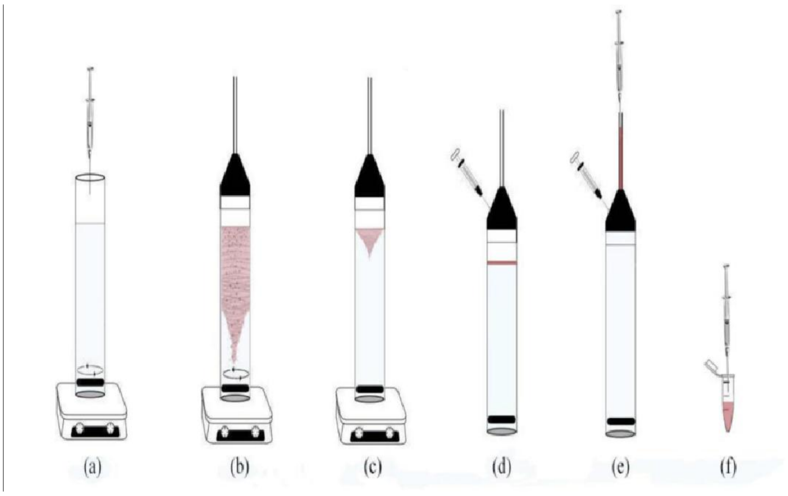

Figure 1. General process of MF-MSA-LLME.

Sample preparation

Water samples were collected from different part of Arak, Iran (river water of Hossein Abad, mineral water of Sarband Mountain, tap and well water of different parts of the city). These water samples were filtered using 0.45 µm micropore membranes, adjusted to the pH of 12 and stored in glass containers at 4 °C.

Results and discussion

In order to achieve the best extraction efficiency of silver ions via micro-funnel magnetic stirring-assisted liquid–liquid micro-extraction (MF-MSA-LLME) method, the influence of different parameters including type and volume of extraction solvent, pH of sample solution, ligand concentration, extraction time and effect of salt were investigated.

Effect of type and volume of extraction solvent

The selection of an appropriate solvent is a key parameter in this purposed method. The extraction solvents should possess densities lower than water, immiscible with aqueous phase, and highest extraction efficiencies for the palladium-PAN complex. For this purpose, 1-undecanol, 1-dodecanol, 1-decanol and n-octanol were tested as extraction solvents. The results revealed that n-octanol has the highest extraction efficiency in comparison with other tested solvents (Figure 2). Therefore, n-octanol was chosen as the best solvent for further studies.

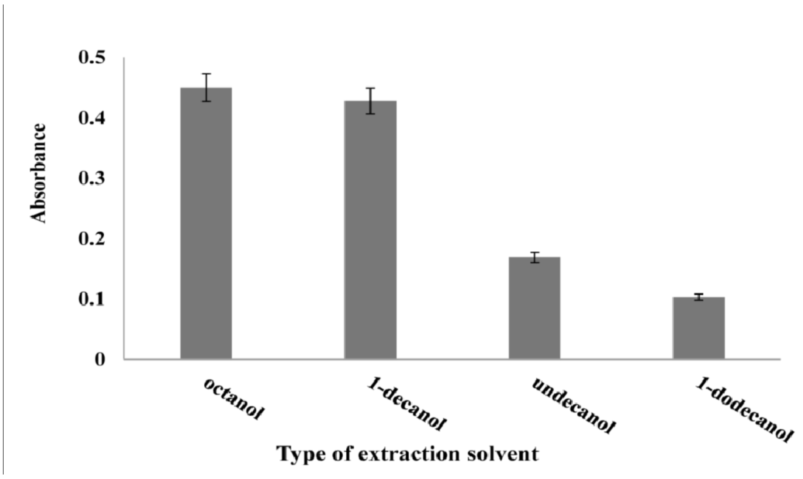

Figure 2. Effect of type of extraction solvent on the MF-MSA-LLME procedure (concentration of Ag 80 µg L^{-1}, pH= 12, $NaNO_3$ concentration 0.1% w/v, extracting= 200 µL PAN solution (300 µg in extraction solvent), extraction time 2 min).

To evaluate the effect of extraction solvent volume, solutions containing different volumes of n-octanol in the range of 100–350 µL were used. According to the results obtained in Figure 3, absorbance of Ag(I) increased up to 200 mL and above this value it decreased.

So, 200 µL of n-octanol was used as the optimum volume of extraction solvent throughout this study.

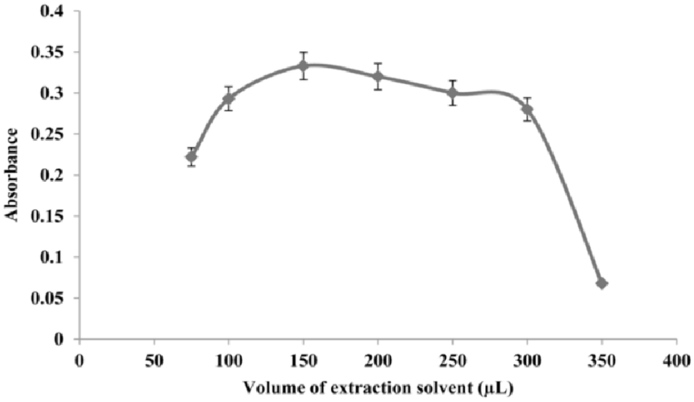

Figure 3. Effect of extraction solvent volume on the MF-MSA-LLME procedure (concentration of Ag 80 µg L^{-1}, pH= 12, $NaNO_3$ concentration 0.1% w/v, extracting= PAN solution (300 µg in n-octanol), extraction time 2 min).

Effect of pH

For the extraction of Ag(I) ions by MF-MSA-LLME method, the complexation and extraction efficiency are closely related to the pH of the sample solution. Therefore, the influence of pH over the range of 9–13 on the Ag(I)–PAN complex formation and the Ag(I) extraction was studied and the results are shown in Figure 4. As it is obvious, the maximum analytical signal was achieved in pH= 12.0. Hence, this pHwas selected for the further studies.

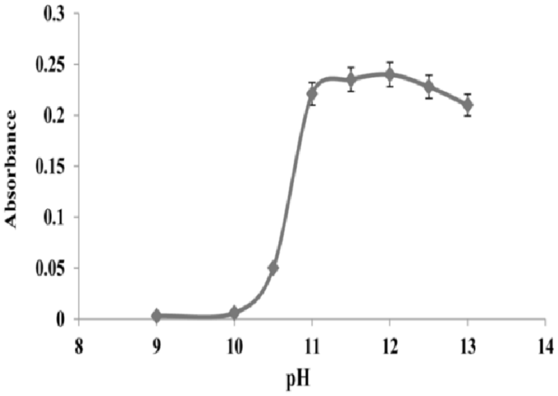

Figure 4. Effect of the pH of sample solution on the MF-MSA-LLME procedure (concentration of Ag 80 µg L^{-1}, $NaNO_3$ concentration 0.1% w/v, extracting= 200 µL PAN solution (300 µg in n-octanol), extraction time 2 min).

Effect of PAN concentration

The influence of PAN concentration on the extraction efficiency of Ag(I) by the proposed method was evaluated. For this purpose, different amount of PAN was dissolved in n-octanol (extraction solvent) at its optimum volume. The obtained results (Figure 5) revealed that the extraction efficiency was increased by increasing the PAN concentration up to 300 µg, and decreased probably due to the extraction of excess of PAN, which decreased the limited capacity of the extraction solvent for the quantitative extraction of the Ag-PAN complex. Thus, 300 µg of PAN was chosen as the optimum amount of ligand for subsequent experiments.

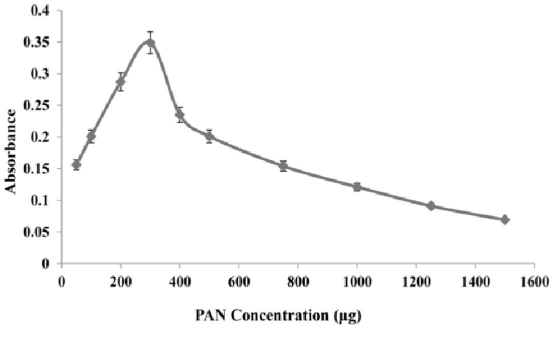

Figure 5. Effect of the PAN concentration on the MF-MSA-LLME procedure (concentration of Ag 80 µg L^{-1}, pH= 12, $NaNO_3$ concentration 0.1% w/v, extracting= 200 µL PAN solution (µg in n-octanol), extraction time 2 min).

Effect of extraction time

The extraction time in MF-MSA-LLME is defined as the interval time between when extraction solvent is injected (n-octanol including 300 µg of ligand) and whenstirrer stage is stopped. In order to study the effect of extraction time, the extraction procedure was done at different time intervals, in the range of 0.5 to 10 min, with the constant experimental conditions and results shown in Figure 6. The results clearly showed that the extraction time has no significant effect on the signal of Ag and the proposed method is very fast. Due to an infinitely large surface area between extraction solvent and aqueous phase, transfer of the Ag-PAN complex into the extraction solvent is rapid. Hence, 2 min was selected as the ideal extraction time for further studies.

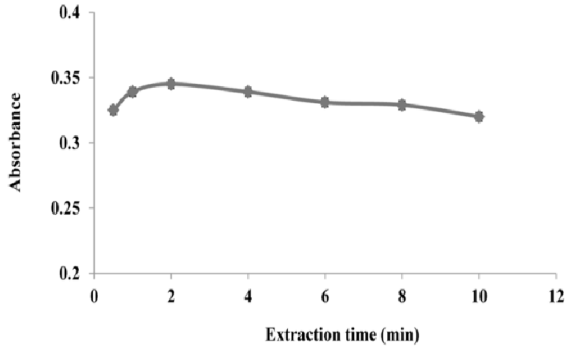

Figure 6. Effect of extraction time on the MF-MSA-LLME procedure (concentration of Ag 80 µg L^{-1}, pH= 12, $NaNO_3$ concentration 0.1% w/v, extracting= 200 µL PAN solution (300 µg in n-octanol)).

Effect of ionic strength

To investigate the influence of ionic strength on the extraction efficiency, different amounts of $NaNO_3$ (0-2% w/v) were examined, while the other experimental conditions were maintained constant. Based on the obtained results (Figure 7), extraction efficiency increased with increasing $NaNO_3$ concentration up to 0.1% and then decreased. So, 0.1% of $NaNO_3$ concentration was chosen for further experiment.

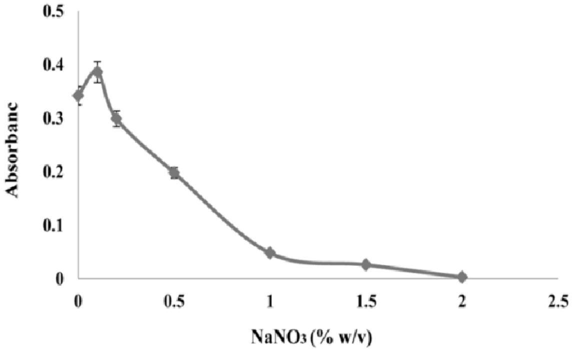

Figure 7. Effect salt on the MF-MSA-LLME procedure (concentration of Ag 80 µg L^{-1}, pH= 12, extracting= 200 µL PAN solution (300 µg in n-octanol), extraction time 2 min).

Effect of interference ions

To evaluate the reliability of the proposed method for the extraction and determination of silver ions, the influence of several added ions on the MF-MSA-LLME and the determination of silver ions were studied. An ion was considered as interfere with relative error of 5%. The results are summarized in Table 1. As is obvious, most of the examined cations and anions at these concentrations had no significant effect on the determination of Ag by the proposed method.

Table 1. Effect of foreign ions on the recovery of 80 µg L^{-1} Ag(I) using MF-MSA-LLME.

Ions	Tolerance limits (µg L^{-1})
K^+, Na^+, Cl^-, NO_3^-, SO_4^{2-}	1000
Ni^{2+}	500
Pb^{+2}	250
Ag^+, Co^{2+}, Zn^{2+}	150
Cu^{2+}, Pd^{2+}, Cd^{2+}	100
Fe^{2+}, Cr^{3+}	50

Analytical figures of Merit

To evaluate the proposed method's performance, the analytical characteristics such as the linear dynamic range, reproducibility, detection limit, and enrichment factor were determined and the results are listed in Table 2. The calibration graph was linear in the Ag (I) concentration range of 2–250 µg L^{-1}, with the equation A = 5.6892 C (µg L^{-1}) - 0.1086 and correlation coefficient (r^2) of 0.997. The limit of detection (LOD) was calculated as the ratio of three times of standard deviation of blank signal and the slop of calibration curve after pre-concentration, was achieved 0.251 µg L^{-1}. The precision of this method was found to be 4% as the relative standard deviation (C=80 µg L^{-1}, n=7). The enrichment factor for the proposed method was found to be 135, as obtained based on the slope ratio of calibration curve after (5.6892) and before (0.0421) of extraction.

Table 2. Analytical characteristics of the proposed method for determination of Ag(I).

Parameter	Value
Regression equation after of extraction	Y = 5.6892X – 0.1086
Regression equation before of extraction	Y = 0.0421X – 0.0098
Linear range (μg L^{-1})	2-250
Correlation coefficient (r^2)	0.997
Enhancement Factor	135
RSD (%) (n=7, Ag^+ concentration=80 μg L^{-1})	4

A comparison of the analytical characteristics of the proposed method for the determination of Ag with some of the best previous methods for this purpose is shown in Table 4. As can be concluded from Table 3, the proposed method has good enrichment factors, wider linear range and low LOD and is comparable with most of the reported methods.

Table 3. Comparison of analytical characteristic of the proposed method with some published method for determination of Ag(I) by FAAS.

Method	LOD (μg L^{-1})[1]	EF/PF[2]	RSD (%)	Reference
SPE	1.05	25	-	[29]
LLE	13	30	2.5	[30]
CPE	1.4	45	2.1	[31]
DLLME	0.41	35	3.1	[32]
SI-DLLME[3]	0.15	186	2.9	[33]
EA-DLLME-FA[4]	2	31	3.4	[8]
USAEME[5]	6.8	10	5.50	[34]
MF-MSA-LLME	0.251	252	4	This work

[1] *LOD: Limit of detection*
[2] *EF: enhancement factor; PF: preconcentration factor*
[3] *SI–DLLME: Sequential injection dispersive liquid-liquid microextraction*
[4] *EA-DLLME-FA: effervescence-assisted dispersive liquid-liquid microextraction based on a medium-chain fatty acid*
[5] *USAEME: Ultrasound-assisted emulsification microextraction*

Analysis of real samples

In order to evaluate the accuracy and applicability of the developed method, it was applied to the determination of Ag from several water samples and the results are summarized in Table 4. For this purpose, 50 mL of each sample was spiked with 40 and 80 μg L^{-1} Ag standard solution and the proposed procedure was followed. As is obvious from Table 4, the extraction efficiency of Ag was excellent, and showed the matrices of the samples did not have serious effects in the determination of Ag by the MF-MSA-LLME method.

Table 4. Analytical results of Ag in environmental water samples.

Sample	Ag added (μg L^{-1})	Found (μg L^{-1})[1]	Recovery (%)
Tap water	0	N.D[2]	-
	40	40.13 ± 1.76	100.32
	80	79.06 ± 1.57	98.82
Well water	0	N.D	-
	40	40.78 ± 1.12	101.95
	80	81.34 ±1.23	101.67
Mineral water	0	N.D	-
	40	41.06 ± 1.98	102.65
	80	78.73 ± 1.88	98.41
River water	0	N.D	-
	40	40.74 ± 1.99	101.85
	80	79.81 ± 1.91	99.76

[1] Mean value of three replicate determination ± standard deviation (n = 3)

[2] Not. Detection

Conclusion

A simple, effective, reliable and economical MF-MSA-LLME method based on application of home-designed extraction vessel coupled with flame atomic absorption spectrometry has been presented for the sensitive determination of silver in water samples. In this work, modified micro-funnel system as a suitable technique is successfully used for easy extraction solvent withdrawal. The magnet stirring was successfully used as a dispersing agent of extraction solvent for pre-concentration of Ag-PAN complex. Unlike the DLLME method, no disperser solvent and centrifugation were used in the proposed procedure. The proposed method has advantages such as low cost, low toxicity, simplicity, rapidity, good enhancement factor, low LOD and high sensitivity and selectivity.

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