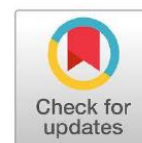




Original Research article

Preconcentration of Silver using Solidification of Floating Organic Drop and Its Determination by Flame Atomic Absorption Spectroscopy



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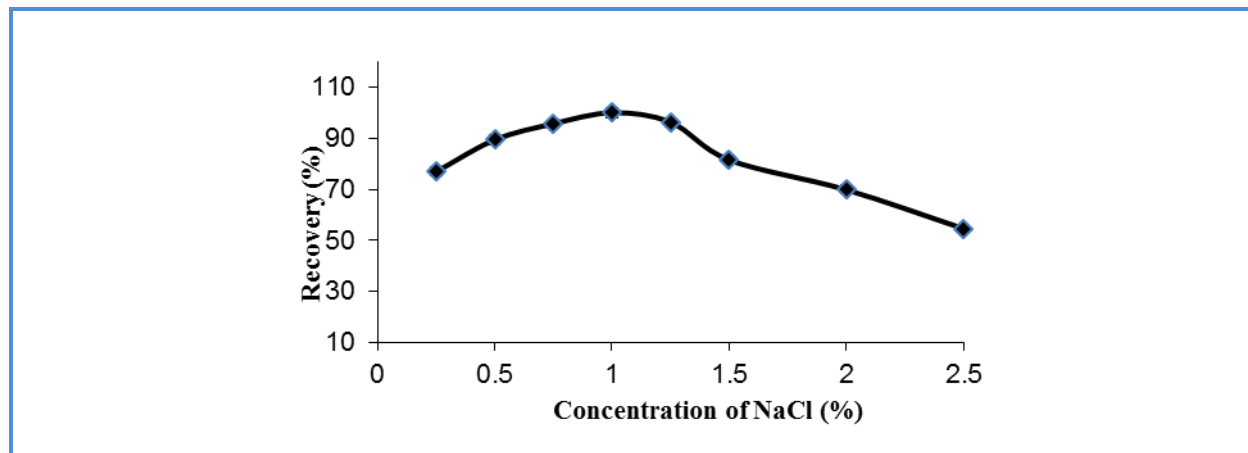
Atomic absorption spectrometry

ABSTRACT

A simple, rapid and dispersive liquid-liquid microextraction-solidification of floating organic drop procedure was combined with flame atomic absorption spectrometry and established for the determination of trace amounts of silver. 5-(4-dimethylamino-benzylidene) (Rhodenylyene) ligand and 1-dodecanol were used as complexing agents and extracting solvents, respectively. The optimum extraction efficiency of silver was obtained after optimization of the pH, concentration of ligand, the nature and amount of solvent extraction, salt increase effect, extraction time, extraction temperature and stirring rate. The effects of various ions on the recovery of Ag were also investigated. The limit of detection defined as $3S_B/m$ was 1.55 ngL^{-1} . The sensitivity for three eight measurements of 10 and $100 \text{ }\mu\text{gL}^{-1}$ of silver was 1.55 ngL^{-1} . The relative standard deviation (RSD) for the measurements of $0.20 \text{ }\mu\text{gL}^{-1}$ of silver was $\pm 2.3\%$. Water well, mineral water and urban drinking water samples were analyzed for Ag amount. The microextraction method was satisfactorily used for the determination of Ag in various environmental waters.

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Graphical Abstract



Introduction

Silver is lustrous, soft, very ductile and malleable metal. It has the highest electrical conductivity of all metals, but it is not widely used for electrical purposes as it is very expensive. Silver is not a chemically active metal; however nitric acid and hot concentrated sulfuric acid will react with it. Silver can be obtained from pure deposits as well as from silver ores such as horn silver and argentite. It can also be obtained as a by-product along with the deposits of ores containing gold, copper, or lead. Silver does not oxidize in air; however it reacts with hydrogen sulfide in the air, causing the metal to tarnish due to the formation of silver sulfide. Hence, silver products require regular cleaning. Silver is stable in water. Dilute solutions of silver nitrate and other silver compounds are used as disinfectants and microbicides (oligodynamic effect), added to bandages and wound-dressings, catheters, and other medical instruments [1].

Separation and preconcentration techniques are commonly used because element concentrations are frequently below instrumental limits of detection. Preconcentration and separation methods such as adsorption, coprecipitation, micellar extraction, liquid-liquid microextraction, electroanalytical separation, and membrane filtration have been studied. A novel microextraction technique, dispersive liquid-liquid microextraction (DLLME), was recently introduced by Assadi and co-workers [2] based on the formation of tiny droplets of the extractant in the sample solution using a water-immiscible organic solvent (extractant) dissolved in a water-miscible organic dispersive solvent. The advantages of the DLLME method are speed, low cost, and high enrichment factors (EFs). However, the required extraction solvent is limited; these solvents, such as chlorobenzene, chloroform, and tetrachloromethane, have a higher density than water and are toxic and environment-unfriendly [3]. In 2007, Yamini and co-workers [4] developed a novel mode of liquid phase microextraction based on the solidification of floating organic

droplets (LPME-SFO), in which a small volume of extractant with low density, low toxicity, and an mp near room temperature (ranging from 10 to 308 C) was used. LPME-SFO has the advantages of LPME of high extraction efficiency, but suffers the same disadvantage as that of DLLME in which centrifugation will be needed to gather the dispersed extraction solvent and separate the organic and aqueous phases, which is time-consuming and restricts the application of LPME in field processing and automated analysis. To overcome the above problem, Leong and Huang [5] combined DLLME and LPME-SFO, developing a new microextraction technique termed as DLLME based on the SFO (DLLME-SFO). In this method, the analysis time can be as fast as that of DLLME and much shorter than that of LPME-SFO. In DLLME-SFO, the appropriate extraction solvent (low density, low toxicity, and proper melting point near room temperature) dissolved in a water-miscible dispersive solvent was rapidly injected into aqueous sample by syringe [6, 7]. A cloudy solution containing fine droplets of the extraction solvent dispersed entirely in the aqueous phase was formed. After centrifugation, the extractant droplet floated on the top of the test tube was easily solidified in an ice bath and then carried out from the aqueous sample to a new test tube where it melted immediately [7, 8]. The melted organic solvent is used for the analytes determination. In this method, the analysis time can be as fast as DLLME and is much shorter than LPME-SFO, and the extractant is of lower density rather than water and lower toxic but higher extraction efficiency for heavy metal ions in contrast to DLLME [9-11]. The aim of this study is to combine DLLME-SFO with FAAS and develop a new method for the determination of Ag content. In this method, 5-(4-dimethylamino-benzylidene) (Rhodanine) was selected as the chelating reagent. All main factors were investigated and optimized. The proposed method was evaluated by analyzing certified reference materials and spiked environmental water samples.

Material and methods

Instrumentation

An atomic Absorption spectroscopy (400 p-nov AA, Analytik Jena, Germany) was used for all the absorption measurements (flow rate acetylene 1.5 liter per minute, flow rate air 3.5 liter per minute, 328.1 nm wave length, and slit width 0.5 nm). All pH measurements were carried out using a digital pH meter model 780 (Metrohm, Switzerland). The solution was stirred with a magnetic heater-stirrer (IKAMAG-RET, Germany). A centrifuge (Sigma Model 3-30K, Germany) was used to accelerate the phase separation process. A simple water bath placed on the heater-stirrer was used for controlling the temperature of the sample solution.

Reagents and solutions

All chemical reagents were of analytical grades, and the deionised water was used for the preparation of all solutions. The 1-dodecanol, silver and phosphate were purchased from Merck Company (Darmstadt, Germany). The other chemicals were prepared from Sigma-Aldrich (St Louis, MO, USA). A stock solution of Ag was prepared from calculated amounts of silver nitrate at a concentration of 1000 milligrams per liter in 0.01 mole per liter HNO₃. Working solutions were prepared daily by appropriate dilution of stock solutions. A solution of 0.02% (w/v) 1-dodecanol as the chelating agent was freshly prepared by dissolving an appropriate amount of it in distilled deionised water.

DLLME-SFO procedure

putting up separate eight milliliters of aqueous solution contained 8.0 µg of silver in a test tube, then we added 1 mL phosphate buffer 0.1 M with pH=0.3, 100 µl of Rudanin 0.05% in ethanol (as disperser solvent), and, finally, we added 1 mL of 1% w/v sodium chloride and mixed thoroughly. Then, 0.25 µl. 1-dodecanol (as extraction solvent) was injected into the sample solution by syringe. The test tube was placed in the ultrasonic sink for 10 min at a temperature of 42 °C. As a result of this, the system appears in cloudy mode due to the spread of fine particles 1-dodecanol within the aqueous solution. Emulsions were then disrupted by centrifugation at 4,000 rpm for 4 min, until very fine droplets of 1-dodecanol, which had a lower density of water and contain silver particles, were placed in a float drop on solution. After this process, the test tube was transferred into an ice bath and the organic solvent solidified after 5 min. The solidified solvent was then transferred into a conical vial where it melted immediately at room temperature. Finally, the extracted organic phase was diluted with 0.5 mL of ethanolic nitric acid and the resulting solution was introduced into the flame atomic absorption spectroscopy and the adsorbents were measured.

Results and discussion

In order to determine silver ions by DLLME-SFOD, several parameters were optimized to achieve a high preconcentration factor and quantitative extraction. So, the influence of different parameters, such as pH, concentration of ligand, the nature and amount of solvent extraction, salt increase effect, extraction time, extraction temperature and stirring rate were investigated. The enhancement factor was calculated as the ratio between the slope ratio of calibration curves obtained after and before DLLME-SFOD.

Effect of pH

The pH of the sample solution is one of the most important factors that affect the formation of complexes and their subsequent extraction. The effect of pH on the DLLME-SFO extraction of Ag was studied in the

pH range of 1.0–9.0. As shown in Figure 1, the highest Ag signal intensity was obtained at pH 2.5–3.5. Therefore, pH 3.0 was selected for the study.

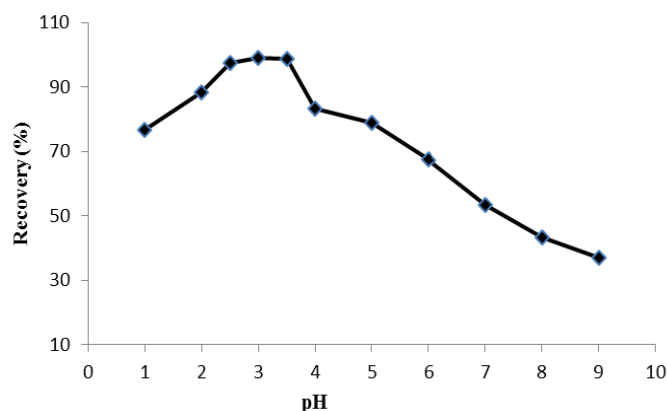


Figure 1. Effect of pH on the extraction of Ag using the DLLME-SFO method

Effect of complexing agent concentration

To extract the ion from the aqueous to organic phase, it is necessary to convert it to an organic aquatic environment by a suitable chelating agent in the form of a hydrophobic complex. In fact, the type and concentration of the caustic agent are those important factors in the extraction, since extraction efficiency in this method depends to a large extent on the hydrophobicity of the complex. Therefore, in the present work, the 5-(4-dimethylamino-benzylidene) (Rhodaniline) ligand in ethanol was used due to suitable refracting and relatively selectable selectivity in the formation of a complex with silver. To investigate this parameter, solutions with concentrations of 1.0 $\mu\text{g}/\text{mL}$ of silver ion were extracted and preconcentrated with different concentrations of Rhodaniline (0.02–0.13%). The percent recovery increases with increasing Rhodaniline content up to 0.04%, fixed up to 0.09% and then decreases. Therefore, the amount of 0.05% ethanol soluble hydrated solution was selected as the optimum amount (Figure 2).

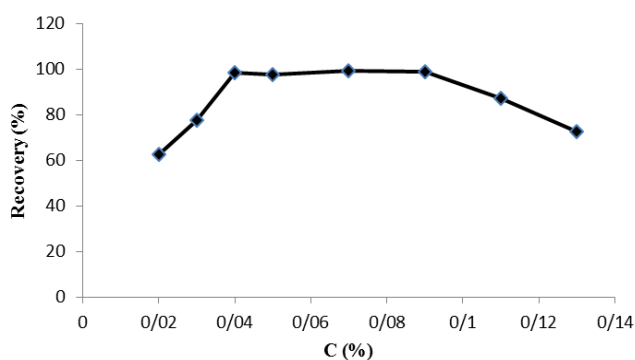


Figure 2. Effect of complexing agent concentration on the extraction of Ag using the DLLME-SFO method

Selection of extracting solvent

The extraction solvent in DLLME-SFO should fulfil the following requirements: this solvent must be immiscible with water and dissolve the analyte better than water to promote the extraction of the analytes. What is more, it should have low volatility, low toxicity, lower density than water, and a low melting point around room temperature (in the range from 10 °C to 30 °C). Therefore, 1-undecanol and 1-dodecanol were studied in the extraction of silver. Some physical properties of the two solvents are listed in Table (1). Solutions of silver at a concentration of 0.8 µg were prepared according to the preconcentration method. According to the results, it is shown that the percent recovery of 1-undecanol and 1-dodecanol is 98% and 97%, respectively. Thus, extraction process is carried out well by both solvents, but due to the lower cost of 1-dodecanol than the other solvent, then this was selected as the extraction solvent.

Table 1. Some physical properties of solvent extraction

Solvent Extraction Type	Extraction Point (°C)	Melting Point (°C)	Density (g/cm ³)
1-Undecanol	243	13-15	0.83
1-Dodecanol	259	22-24	0.83

Effect of extraction solvent volume

To evaluate the effect of the extraction solvent volume, different volumes of 1-dodecanol in the range of 15–50 µL (at 5 µL intervals) were examined in the preconcentration procedure. The results illustrated in Figure 2 show that, by increasing the volume of 1-dodecanol, the analytical signal increases, reaching a maximum value at 25 µL and then remaining constant. Therefore, in the subsequent studies, 25 µL was used as the optimum volume of the extraction solvent (Figure 3).

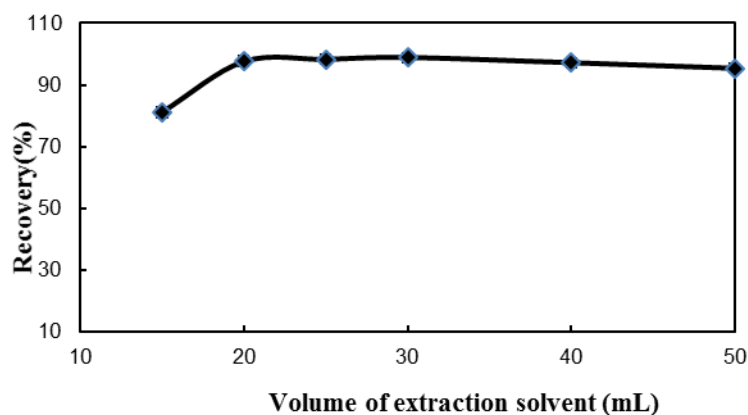


Figure 3. Effect of the volume of extraction solvent on the extraction of silver by the DLLME-SFO method

Effect of extraction temperature

Temperature can affect the mass transfer process and consequently the extraction efficiency. The effect of extraction temperature was investigated on 0.88 mL of aqueous solution, containing 0.8 μg of silver ion at a temperature range of 30-60 °C. According to the results, the highest extraction efficiency was obtained at a temperature range of 40-45 °C. Therefore, the temperature 42 °C was used for further study.

Effect of extraction time

Extraction time is also an important factor in DLLME-SFO as in most other extraction procedures. In the DLLME-SFO, the extraction time was defined as the time interval elapsed between the start of addition of the mixture of extraction solvent and dispersive solvent to the sample and the time before centrifugation. The effect of extraction time on the extraction efficiency was examined by varying the extraction time from 5 to 20 min. The extraction efficiency was obtained from 7.5 to 12.5 min. Therefore, the time of 10 min was used as extraction time in subsequent experiments. This means that the equilibriums of both the metal-chelate reaction and the extraction process can be achieved quickly.

Effect of stirring rate

The stirring rate is an important parameter that enhances the kinetics of chelate formation and its extraction. According to the film theory of convective-diffusive mass transfer in the LPME system, faster sample agitation causes lower thickness of diffusion film in the aqueous phase. The optimum stirring rate was evaluated at different stirring rates, between 1000 and 6000 rpm at a constant extraction time of 4 min. As shown in Figure 3 up to 4000 rpm, the absorbance signal rose as the stirring rate was increased. Afterwards, it remained constant. Higher stirring rate were not used, because at such rates, the spattering damaged the micro drops. Hence, a stirring rate of 4000 rpm was adopted for subsequent experiments.

Effect of salt

To investigate the salt effect on the performance of DLLME-SFOD, various experiments were performed by adding different amounts of sodium chloride (0.25-2.5%). By increasing the amount of salt from 0.75 to 1.25% (w/v), the absorbance increased. Therefore, the salting out effect decreased the solubility of the extraction solvent in the aqueous phase and increased the enrichment factor. When larger amounts 1.25% (w/v) of sodium chloride were added, the volume of the floating phase increased because of decreased solubility of floating solvent in the aqueous

phase, which decreased the enrichment factor slightly (Figure 4). This is one of the good properties of this method for analyses of real sample.

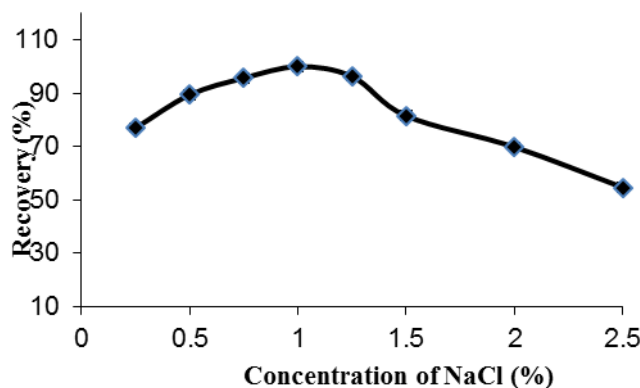


Figure 4. Salting out effect on silver percent recovery

Analytical figures of merit

The analytical characteristics of the proposed method, such as linear range, limit of detection, reproducibility and correlation coefficient obtained by processing standard solutions of Ag under the optimum conditions described are summarized in here. The calibration graph was linear in the range of 8.0–3000.0 ngL⁻¹ of silver. The equation of the calibration curve after the preconcentration procedure was given as $A = 0.2549C + 0.0026$ with a correlation coefficient of 0.9957, where A is the atomic absorbance for silver in the rich phase and C is the concentration of Ag ions in the sample solution in micrograms per liter. The limit of detection defined as $3S_B/m$ (where S_B is standard deviation of the blank and m is the slope of the calibration graph) was 1.55 ngL⁻¹. By definition, sensitivity to the atomic absorption spectrum is the concentration of the element that absorbs one percent of the radiation. The sensitivity for three eight measurements of 10 and 100 µg/L⁻¹ of silver was 1.55 ngL⁻¹. The relative standard deviation (RSD) for measurements of 0.20 µg/L⁻¹ of silver was ±2.3%.

Effect of interfering ions

Due to the high selectivity of the DLLME-SFOD, the possible interferences can mostly be ascribed to the preconcentration step. In order to indicate the selectivity of the method, the effect of several common ions present in environmental and biological samples for the determination of 0.2 µg/L⁻¹ of Ag was tested. For this purpose, to 8 mL of standard solutions of silver containing 8.0 mg of silver, various amounts of various cations and anions were added. Then it's pre-concentrated and

measured according to the method of study. The tolerance limit of coexisting ions was defined as the largest amount producing a variation of less than 5% in the recovery of analytes. The tolerance limits of diverse ions are given in Table 2. The results indicated that the presence of the ions at the mole ratio shown in Table 2 has no significant effect on the extraction of analytes.

Table 2. Investigating the effects of interfering ions on silver adsorption

Ions	Mole Ratio (Ion/analytes)	Percent Recovery
PO ₄ ³⁻ , H ₂ PO ₄ ⁻ , HPO ₄ ²⁻	> 5000	95.0
Co ²⁺	700	95.0
Ni ²⁺	600	98.0
Mn ²⁺	500	105.0
Cu ²⁺	400	105.0
Pb ²⁺	500	95.0
Cd ²⁺	600	96.0
Pd ²⁺	600	104.0
Rh ³⁺	800	105.0
Zn ²⁺	300	95.0
Fe ³⁺	100	96.0
Al ³⁺	50	95.0

Analysis of natural waters

To examine the accuracy of the proposed procedure, the method was applied to the determination of analytes in water well, mineral water and urban drinking water. The results, along with the recovery (for spiked samples), are given in Table 3. The recoveries for the addition of different Ag concentrations to water samples were in the range 98.0–106.0%. To verify the accuracy of the proposed procedure, the method was used for the determination of Ag in a sample of mineral water, water well and urban drinking water. The results of this test are presented in Table 3. Good agreement between the determined and certified values was obtained.

Table 3. Determination of Ag in three kind of environmental water samples and relative recovery of spiked Ag in environmental water samples

sample	Added	Found	Recovery (%)
Water Well	0.0	>LOD	---
	10.0	9.8±0.3	98.0
Mineral Water	0.0	>LOD	---
	10.0	10.6±0.4	106.0
Urban Drinking Water	0.0	>LOD	----
	10.0	10.4±0.4	104.0

Comparison to other methods

The performance of the presented DLLME-SFO method was compared with the other reported methods (the relevant data are listed in Table 4). As can be seen from Table 4, the DLLME-SFO

method has comparable linearity range, LODs and RSDs with, and in some cases is better than those of the other reported extraction methods. However, it requires much shorter extraction time than either CPE or LL-DLLME. Furthermore, this DLLME-SFO is easy to operate without the need of any special instruments. The method is indeed simple, efficient, and environmentally friendly, and could be suitable for the routine analysis of the trace Ag ions in water and beverage samples. In other hands the results of the investigation indicate that solidified floating organic drop micro extraction (SFODME) combined with flame atomic absorption spectrometry can be used as a simple and powerful technique for pre-concentration and determination of metal ions in aqueous samples.

Table 4. Comparison of the proposed method with other methods for pretreatment and determination of silver

Methods	DL (ng/mL ⁻¹)	RSD (%)	LDR (ng/mL ⁻¹)	Ref
LL-DLLME-FAAS	1.2	1.5	5-2000	[12]
CPE-ETAAS	1.2	4.2	5-100	[13]
CPE-FAAS	1.4	2.1	---	[14]
CPE-FAAS	2.2	2.6	10-200	[15]
DLLME-SFO	1.55	2.3	8-3000	Proposed method

Conclusions

In this paper, a DLLME-SFO method was described for preconcentration and determination of silver. This technique provides good precision, simplicity, ease of operation, low LOD, linearity over a wide range, and good recovery within a short time (a few s) as compared to other techniques. Moreover, it uses an extraction solvent with lower toxicity instead of a solvent with high toxicity, as in DLLME, and it is faster than SFODME. The method does not require any additional specific equipment or training for performing the extraction, so it is inexpensive. The performance of this procedure in the extraction of Ag ions from different real samples with various matrixes is excellent.

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