



Application of Dispersive Liquid-Liquid Microextraction in Separation and Preconcentration of Silver prior its Determination by Flame Atomic Absorption Spectrometry

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Abstract. A simple, sensitive, and rapid dispersive liquid-liquid microextraction (DLLME) method is developed for the preconcentration of silver ions prior to determination by flame atomic absorption spectrometry (FAAS). In this work, 1-phenyl-1,2-propanedione-2-oximethiosemicarbazone (PPDOT), chloroform, and methanol are used as the complexing agent, extraction solvent, and disperser solvent, respectively. The effects of different analytical parameters on the complex formation and the extraction efficiency are investigated and optimized. The effects of interfering ions on the determination of silver(I) are also examined. Under the optimized conditions, a linear calibration curve was achieved in the range of 0.60–120.0 $\mu\text{g L}^{-1}$, with the detection limit of 0.61 $\mu\text{g L}^{-1}$. The pre-concentration factor calculated as the ratio of the slopes of the calibration graphs with and without the pre-concentration was 35.5. The relative standard deviations (RSDs) for the silver(I) determinations were below 3 %. The proposed separation procedure was successfully applied to the determination of silver(I) in natural water and photographic film samples with satisfactory results (recoveries > 95 %).

Keywords: silver, 1-phenyl-1,2-propanedione-2-oximethiosemicarbazone, dispersive liquid-liquid microextraction (DLLME), flame atomic absorption spectrometry (FAAS)

INTRODUCTION

Many applications of silver and silver compounds in life, medicine, and industry have resulted in an increasing silver content of environmental samples. Silver compounds and alloys attend in photographic films, mirrors, coins, jewelry, and dental and pharmaceutical preparations.^{1,2} Also because of its anti-microbial features, it is impregnated in filters used in the disinfection of drinking or swimming pool waters, and in the processing of foods and drugs.^{3,4} It can go into the environment through industrial wastes and create health problems as a water pollutant. However, a silver ion concentration up to 0.1 mg L^{-1} is usually not hazardous for human health.¹ In this regard, the determination of silver is important in many environmental samples including natural waters.⁵

Various analytical techniques have been used for determination of silver in different environmental samples in the flame atomic absorption spectrometry

(FAAS),^{6–8} graphite furnace-atomic absorption spectrometry (GF-AAS),^{9,10} inductively coupled plasma-mass spectrometry (ICP-MS),^{11–13} inductively coupled plasma-atomic emission spectrometry (ICP-AES),¹⁴ and stripping voltammetry.^{15,16} In particular, FAAS due to its short analysis time, relative simplicity, and low cost is being one of the most commonly applied methods for the determination of trace amounts of metal ions in a variety of environmental samples. However, the main problems with this technique are matrix effect and its relatively poor sensitivity for some metal ions, meaning that it cannot determine metals at the $\mu\text{g L}^{-1}$ level. Therefore, to improve FAAS sensitivity, preconcentration and separation procedures are required. Several methods including liquid-liquid extraction (LLE),^{17–19} co-precipitation,^{20,21} cloud point extraction (CPE),^{22,23} membrane filtration²⁴ and solid-phase extraction (SPE)^{25,26} have been reported for pre-concentration and/or separation of the analyte from the interferences. However, these methods suffer from the drawbacks

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such as time-consumption, poor enrichment factors, and large volumes of toxic organic solvents.⁷ To overcome these problems, modern analytical methods including LPME^{27–30} and solid phase microextraction (SPME)^{31,32} have been introduced and developed. LPME can be divided into three chief types: single-drop microextraction (SDME),^{33,34} hollow-fiber-based liquid phase microextraction (HF-LPME)³⁵ and dispersive liquid-liquid microextraction (DLLME).^{36–39} However, SDME and HF-LPME have disadvantages including low stability of liquid drop in SDME,⁴⁰ formation of air bubbles in HF-LPME,⁴¹ and long analysis time.²⁹ To overcome these problems, DLLME has been developed.

DLLME is based upon a ternary component solvent system. In DLLME, an appropriate homogeneous mixture of water-immiscible extraction solvent and water-miscible disperser solvent is rapidly injected into an aqueous sample containing the analyte with the aid of a syringe. As a result, a cloudy solution is formed, and the analyte in the sample is extracted into fine droplets of the extraction solvent. Due to the enlarged surface area between the organic phase (extraction solvent) and the aqueous phase, the extraction process happens very quickly, and so, equilibrium state is attained very fast. Therefore, a very short extraction time is obtained. After extraction, centrifugation is performed for phase separation, and the sedimented phase containing the analyte at the bottom of the conical test tube is removed manually by a microsyringe. Finally, the preconcentrated analyte in the sedimented phase is determined by one of the analytical techniques such as high-performance liquid chromatography (HPLC),³⁸ gas chromatography (GC),⁴² FAAS, and GF-AAS. Recently, DLLME has been applied as a separation / preconcentration method for organic and inorganic compounds from water samples.^{36,39,43–47} Operation simplicity, rapidity, small values of the organic solvent, low cost, and large enrichment factor and recovery are the main advantages of this extraction method.

1-Phenyl-1,2-propanedione-2-oximethiosemicarbazone (PDOT), as a chromofore reagent, reacts with some heavy metal ions as well as Ag(I). PPDOT is used in the UV-visible spectrophotometric determination of Ag(I).^{47,48} Ag(I)-PPDOT complex formation is kinetically independent from time. In the present work, DLLME is proposed for the separation and pre-concentration of Ag(I) ions prior to their FAAS determination. Because of the well-documented selectivity of PPDOT towards silver ions,⁴⁸ this ligand was used as a complexing agent. Also this procedure was successfully applied to the determination of silver in water and photographic film samples for the first time.

EXPERIMENTAL

Apparatus

A Shimadzu Model AA-670 (Kyoto, Japan, <http://www.shimadzu.com>) flame atomic absorption spectrometer equipped with deuterium background correction and silver hollow cathode lamp was utilized for atomic absorption measurements at the wavelength of 328.1 nm. The equipment parameters were adjusted according to the standard conditions recommended by the manufacturer. To record UV-visible spectra of the complex and the ligand, a Ray Leigh UV 2601 (London, England, <http://www.rayleigh.co.uk>) spectrophotometer with 1.0 cm quartz cells was used. A Benyamin Teb centrifuge (Tehran, Iran) was utilized for the phase separation. The pH values were measured using a Metrohm Model 744 (Herisau, Switzerland, <http://www.metrohm.com>) digital pH-meter supplied with a glass-combined electrode. An adjustable sampler (1–100 μL) was prepared from Eppendorf (Hamburg, Germany, <http://www.eppendorf.com>).

Chemicals

All the chemicals used were of analytical-reagent grade. Doubly distilled water was used in the preparation of all aqueous solutions. The stock standard solutions of Ag(I) at a concentration of 1000 $\mu\text{g mL}^{-1}$ was obtained by dissolving an appropriate amount of silver nitrate (Merck, Darmstadt, Germany, <http://www.merck.com>) in doubly distilled water containing 2 mL of concentrated nitric acid (Merck). This solution was standardized by a known titration method 49 and stored in the dark. The working standard solutions of Ag(I) were prepared daily by stepwise dilution from the stock solution. A solution of 20.0 $\mu\text{g L}^{-1}$ of Ag(I) was used in these investigations. A solution of 0.0050 mol L^{-1} PPDOT was prepared by dissolving an appropriate amount of PPDOT in N,N-dimethylformamide (Merck). Carbon tetrachloride, chloroform, 1,2-dichlorobenzene and dichloromethane were purchased from Merck and used as the extraction solvents. Also methanol (Merck), acetonitrile (Merck), ethanol (Kiankavehazma, Tehran, Iran), and acetone (Kiankavehazma) were used as the disperser solvents. The other chemicals used were obtained from Merck. Buffer solutions with the pH range of 2.0–8.0 were obtained by mixing appropriate volumes of the solutions of K_2HPO_4 (0.10 mol L^{-1}), $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (0.10 mol L^{-1}), and H_3PO_4 (0.10 mol L^{-1}). Acetate buffer solution of pH 5.0 was prepared by mixing the solutions CH_3COONa (0.10 mol L^{-1}) and CH_3COOH (0.10 mol L^{-1}). Citrate buffer solution with pH 5.0 was obtained by mixing the solutions $\text{C}_6\text{H}_5\text{O}_7\text{Na}_3 \cdot 2\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$. The pH

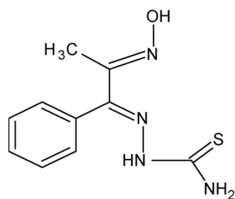


Figure 1. Structure of PPDOT.

values of the above buffer solutions were controlled by the pH-meter during their preparation. To investigate the interference effects of cations and anions, several solutions of metal salts and alkali metal salts were prepared and used, respectively.

Preparation of PPDOT

The PPDOT ligand was prepared by simple condensation of 1-phenyl-1,2-propanedione-2-oxime with thiosemicarbazide according to the formerly reported method.⁴⁷ Structure of the ligand PPDOT is shown in Figure 1.

DLLME Procedure

Under the optimum conditions, an aliquot of 10.0 mL of aqueous samples or standard solutions containing $20.0 \mu\text{g L}^{-1}$ of Ag(I), $0.50 \mu\text{g L}^{-1}$ of PPDOT, and an acetate buffer (pH 5.0) was placed in a screw cap glass test tube with a conical bottom. Then a mixture of methanol (750.0 μL) and chloroform (200.0 μL) was injected rapidly into the sample solution with the aid of a 2 mL syringe with a stainless needle. As a result, a cloudy solution was formed in the test tube. This solution was softly shaken for five times. At this stage, silver ions were reacted with the ligand PPDOT and the interior of the fine droplets of chloroform were extracted. Then the cloudy solution obtained was centrifuged at 5000 rpm for 5 min, and the chloroform phase containing Ag(I) was sedimented at the bottom of the conical test tube. Afterwards, 100.0 μL of the sedimented phase was transferred into a vial with conical bottom using a 100 μL microsyringe and diluted by ethanol to 200.0 μL . To determine silver, the final solution was directly aspirated into the flame atomic absorption spectrometer.

Sample Preparation

A seawater sample was collected from the Caspian Sea near the Babolsar Coast, and two tap water samples were collected from Shahrood and Jajarm were located in Eastern North of Iran. All seawater samples were filtered through 0.45 μm of pore size membrane filters to remove the suspended particulate matter and stored in a pre-cleaned polyethylene bottle. Before analysis, the sample was adjusted to optimum pH value of 5.0 using an acetate buffer solution.

For determination of silver in the photographic film sample, it was prepared according to the reported process.⁷ In this process, the photographic film sample was washed with doubly distilled water, dried in oven at 40 °C for 20 min, and cut into small pieces. Then 0.01 g of pieces of film was weighed, and 5.0 mL of nitric acid (4.0 mol L^{-1}) was added to them. The mixture was filtered, the solution was diluted to the volume of 100.0 mL, and the pH was adjusted at 5.0 using NaOH (0.10 mol L^{-1}). Finally, 5.5 mL of the prepared sample solution was removed, and the silver amount was determined according to the reported method.

RESULTS AND DISCUSSION

In this work, the possibility of combination of DLLME with FAAS for determination of trace amounts of silver was investigated. The effects of various experimental parameters influencing complex formation and its subsequent extraction such as pH, type and volume of buffer, type and volume of extraction solvent, type and volume of disperser solvent, ligand concentration, volume of aqueous sample, extraction time, centrifugation time, and ionic strength were optimized using one variable at a time optimization. The solution of $20.0 \mu\text{g L}^{-1}$ Ag(I) was used in these investigations. The ER % can be calculated from equation (1):

$$\text{ER \%} = \frac{C_{\text{sed}} V_{\text{sed}}}{C_0 V_{\text{aq}}} \cdot 100 \quad (1)$$

where C_{sed} and C_0 are the analyte concentrations in the sedimented phase and the initial analyte concentration in the aqueous sample, respectively. Also V_{sed} and V_{aq} are the volumes of the sedimented phase and the aqueous sample, respectively.

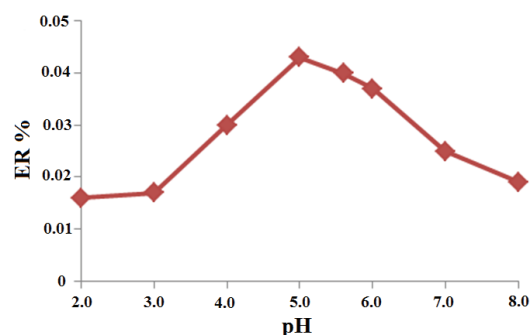


Figure 2. Effect of pH on the extraction recovery of Ag(I). Conditions: Ag(I): $20.0 \mu\text{g L}^{-1}$; PPDOT: $1.6 \times 10^{-4} \text{ mol L}^{-1}$; aqueous sample volume: 10.0 mL; extraction solvent (chloroform) volume: 200.0 μL ; disperser solvent (acetone) volume: 800.0 μL .

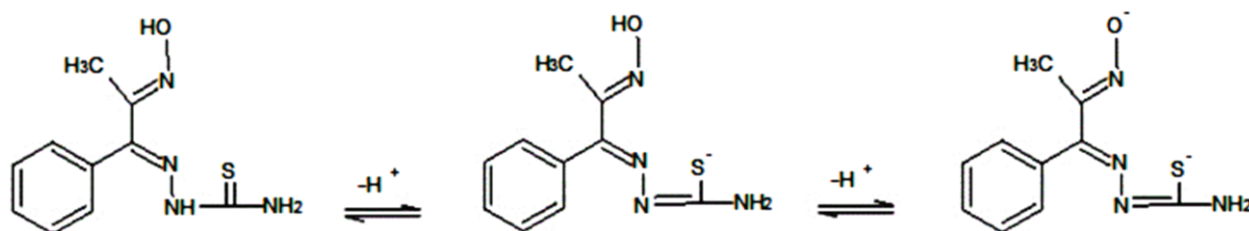


Figure 3. Forms of PPDOT in different pH ranges.

Effect on pH

The pH plays an important role on the complex formation and its extraction into the organic phase. In this study, the effect of pH on DLLME of Ag(I) was investigated in the pH range of 2.0–8.0 using phosphate buffers. Figure 2 shows that maximum extraction recovery for Ag(I) using DLLME was obtained at pH 5.0. At lower pH values, electron donor groups in the ligand PPDOT are protonated, and so, complex formation in the aqueous phase is decreased. Also at these pH values, the Ag(I)-PPDOT complex has a positive charge, and cannot be extracted into the organic phase. Thus ER % decreases at lower pH values. As pH increases, the ligand PPDOT changes into the tautomeric form, and the complex converts to neutral (see Figure 3). Thus it can be extracted into the organic phase. At higher pH values, the complex has a negative charge and cannot be extracted into the organic phase. Also ER % diminishes at higher pH values, since hydroxy species compete with the ligand species to react with Ag(I) ions. Thus pH 5.0 was selected as the optimal pH value for the further experiments. Also the effect of buffer type on extraction recovery (ER %) was investigated using the phosphate, acetate, and citrate buffer solutions in the same pH and concentration. The results obtained showed that maximum recovery was achieved when the acetate buffer was used. Probably, due to reaction of Ag(I) with phosphate in the presence of phosphate buffer and reaction of Ag(I) with citrate in the presence of citrate buffer, Ag(I)-PPDOT complex formation decreases. Hence, all the standard and sample solutions were buffered by addition of 2.0 mL of acetate buffer (0.10 mol L^{-1}) at pH 5.0.

Selection of Extraction Solvent

Extraction solvent must own a higher density than the aqueous phase, low solubility in water, and a high extraction capacity. For this purpose, some organic solvents such as chloroform, carbon tetrachloride, dichloromethane, and 1,2-dichlorobenzene were utilized. For this work, several sample solutions containing Ag(I) were examined using 800.0 μL of acetone (as the disperser solvent) and 200.0 μL of various extraction solvents. It was observed that a very low volume of

sedimented phase was achieved when dichloromethane was used. Furthermore, the fine cloudy solution was not formed by using this solvent. The results obtained show that a maximum extraction recovery was obtained when chloroform was used as the extraction solvent. It seems that solubility of the complex in chloroform is higher than that in the other solvents. Therefore, chloroform was selected as the extraction solvent for the next investigations.

Selection of Disperser Solvent

In the DLLME procedure, the disperser solvent must be miscible in both the organic phase (extraction solvent) and sample solution (aqueous phase). Actually, the disperser solvent works as a bridge to disperse the extraction solvent into the sample solution. For this aim, some different solvents such as ethanol, methanol, acetone, and acetonitrile were used. A series of sample solutions were tested using 800.0 μL of each one of these solvents containing 200.0 μL of chloroform as the extraction solvent. It was found that the volume of the sedimented phase was lower in comparison with the other disperser solvents. ER % for ethanol, methanol, acetone, and acetonitrile were obtained to be 15.5, 71.8, 40.4, and 50.5 %, respectively. According to the results obtained, maximum extraction recovery was obtained when methanol was used as the disperser solvent. Also the better and more stable cloudy solution was

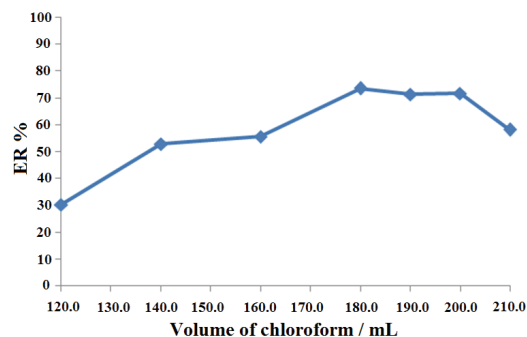


Figure 4. Effect of extraction solvent volume on the extraction recovery of Ag(I). Conditions: Ag(I): $20.0 \mu\text{g L}^{-1}$; PPDOT: $1.6 \times 10^{-4} \text{ mol L}^{-1}$; aqueous sample volume: 10.0 mL; disperser solvent (methanol) volume: 800.0 μL .

formed when methanol was used. Therefore, this solvent was chosen as the disperser solvent for the further studies.

Effect of Extraction Solvent Volume

In order to study the effect of the extraction solvent volume on the extraction recovery, a series of solutions containing different volumes of chloroform with a fixed volume of methanol (800.0 μL) were subjected to the DLLME procedure. It was observed that by increasing the chloroform volume from 120.0 to 210.0 μL , the sedimented phase volume increased from 50.0 to 140.0 μL . As it could be seen in Figure 4, the recovery percent is almost constant with increase in the chloroform volume from 180.0 to 200.0 μL , and then decreases. Reduction in recovery was observed above 200.0 μL , probably because of the decrease in the ratio between the volume of the disperser solvent and the volume of the extraction solvent. This reduced ratio decreases the possibility of dispersion of the extraction solvent droplets into the sample solution by the disperser solvent, and thus the extraction efficiency diminishes. Thereby, 200.0 μL of chloroform was used as the optimized volume of the extraction solvent for the subsequent experiments.

Effect of Disperser Solvent Volume

Effect of the disperser solvent volume on the extraction recovery of silver was also studied. For this work, several solutions containing a constant volume of chloroform (200.0 μL) dissolved in different volumes of methanol (400.0–1000.0 μL) were tested by the DLLME procedure. The results obtained (Figure 5) show that ER % increases with increase in the methanol volume from 400.0 to 800.0 μL , and then it decreases in the volumes above 800.0 μL . In lower volumes of methanol, due to the low ratio of the volume of the disperser solvent and the volume of the extraction

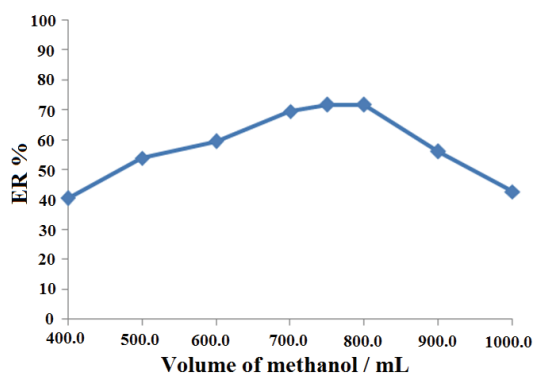


Figure 5. Effect of disperser solvent volume on the extraction recovery of Ag(I). Conditions: Ag(I): 20.0 $\mu\text{g L}^{-1}$; PPDOT: 1.6×10^{-4} mol L^{-1} ; aqueous sample volume: 10.0 mL; extraction solvent (chloroform) volume: 200.0 μL .

solvent, formation of small droplets may not be effective.⁷ Furthermore, an adequate volume of methanol to disperse the chloroform as the extraction solvent into the aqueous phase may not be available. In the volumes above 800.0 μL , probably increased solubility of the complex in aqueous phase leads to reduction in the extraction recovery. Thus 750.0 μL of methanol was used as the optimized value of the disperser solvent for the subsequent experiments.

Effect of PPDOT Concentration

Influence of the PPDOT concentration as the complexing agent for the pre-concentration and extraction of silver was evaluated. In this part, different concentrations of PPDOT in the range of 4.0×10^{-5} – 1.1×10^{-3} mol L^{-1} were prepared in DMF. According to the results obtained (Figure 6), the recovery enhances by increase in the PPDOT concentration up to 3.0×10^{-4} mol L^{-1} , and then from 7.0×10^{-4} mol L^{-1} , it decreases due to extraction of the free PPDOT molecules instead of the Ag-PPDOT complex. Hence, the concentration of 5.0×10^{-4} mol L^{-1} was selected as the optimized concentration of PPDOT to avoid any interference on the Ag(I) microextraction.

Effects of Extraction Time and Ionic Strength

Extraction time in DLLME is described as the interval time between injection of the mixture solvents (the extraction solvent and the disperser solvent) and start of centrifugation. Effect of centrifugation time was evaluated within the range of 1–30 min with the fixed experimental conditions. The results obtained indicated that extraction time had no remarkable effect on the extraction efficiency. Since after formation of cloudy solution, the surface area between the extraction solvent and the aqueous phase is extremely increased and complex diffusion into the extraction solvent is fast, and

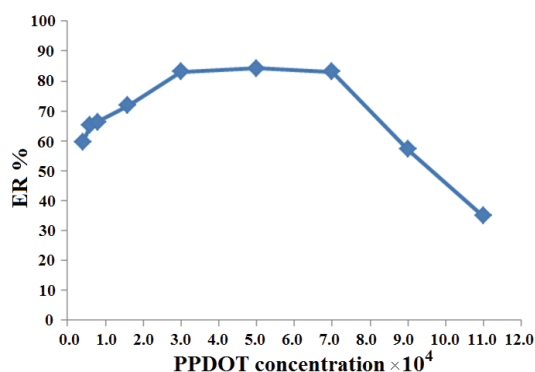


Figure 6. Effect of PPDOT concentration on the extraction recovery of Ag(I). Conditions: Ag(I): 20.0 $\mu\text{g L}^{-1}$; aqueous sample volume: 10.0 mL; extraction solvent (chloroform) volume: 200.0 μL ; disperser solvent (methanol) volume: 750.0 μL .

equilibrium state is obtained rapidly. Short extraction time is the most notable advantage in the DLLME procedure.

The effect of ionic strength on the extraction efficiency of silver was also investigated. In this study, different concentrations of KNO_3 ($0.00\text{--}0.60 \text{ mol L}^{-1}$) were added to the sample solutions containing silver ion, while other experimental conditions were fixed. According to the obtained results, ionic strength has no significant effect on recovery. Thus the following studies were accomplished with no salt addition.

Effect of Matrix Ions

The effect of diverse foreign ions on DLLME of silver was investigated under the optimized conditions. In this study, solutions containing $20.0 \mu\text{g L}^{-1}$ of Ag(I) and the interfering ions with various interference-to-analyte ratios ($w_{\text{ion}} / w_{\text{Ag(I)}}$) were pre-concentrated and deter-

Table 1. Effect of the matrix ions on the recovery of silver(I) ion ($n = 3$)

Foreign ion	Tolerance limit ($w_{\text{ion}} / w_{\text{Ag(I)}}$)	Recovery / %
Li^+ , F^- , H_2PO_4^-	10000	103.0
Mn^{2+} , SCN^-	10000	101.5
K^+ , Mg^{2+} , Ba^{2+} , NO_2^- , SO_4^{2-} , Cl^- , citrate	10000	99.5
HPO_4^{2-}	10000	98.0
SO_3^{2-}	10000	97.0
Na^+ , NO_3^- , PO_4^{3-} , HCO_3^-	10000	95.5
$\text{C}_2\text{O}_4^{2-}$	10000	94.5
Ca^{2+}	10000	93.0
HSO_4^-	5000	101.5
Br^-	5000	95.5
Cr^{3+}	1000	103.0
CH_3COO^-	1000	100.5
Pb^{2+} , Cd^{2+}	1000	97.0
$\text{S}_2\text{O}_5^{2-}$	1000	94.5
I^-	1000	93.0
Zn^{2+}	800	93.0
Fe^{3+}	500	100.5
Fe^{2+}	500	97.0
CN^-	100	104.0
Co^{2+}	100	99.5
Cu^{2+}	100	98.0
Hg^{2+}	100	97.0
Ni^{2+}	100	93.0
Al^{3+}	20 (800 ^(a))	97.0 ^(b)

^(a) Tolerance limit after treatment with 100 mg L^{-1} of F^- ions.

^(b) Recovery (%) after treatment with 100 mg L^{-1} of F^- ions.

mined using the proposed procedure. The tolerance limit for a foreign ion was obtained as the value that resulted in the deviation of absorbance value more than $\pm 3\sigma$ (σ is the standard deviation of three replicate measurements of absorbance for solution containing $20.0 \mu\text{g L}^{-1}$ of Ag(I)).

First the signal for the sample solution in the absence of foreign ions was measured. Then extraction was performed on this solution under the optimal conditions. The analytical signal obtained was measured six times, and the mean signal and standard deviation were calculated. Acceptable range for signal swing was obtained according to $\sigma \pm 3\sigma$. Then to investigate any possible interference effect, the interfering species with the concentration of 10000 times the analyte concentration was added to the initial solution. After microextraction of silver complex to the organic drop, the analytical signal was measured. If in the presence of a foreign ion, the signal is located in $\sigma \pm 3\sigma$, this means that the desired ion does not have any effect as interference in this procedure. Otherwise, the weight ratio of the interfering species was reduced in order to put the analytical signal in the $\sigma \pm 3\sigma$ range. The results obtained (Table 1) indicate that all the studied ions except Al(III) have no significant interference effect on the determination of Ag(I) . The interference effect of Al(III) can be decreased up to 800-fold by addition of 100 ppm of fluoride (NaF) as the masking agent. However, this cation did not interfere with the determination of Ag(I) when different real samples were investigated.

Figures of Merit

The analytical performance characteristics of the proposed method under the optimized conditions are shown in Table 2. For a sample volume of 10.0 mL, the optimum linear concentration range for Ag(I) was $0.60\text{--}120.0 \mu\text{g L}^{-1}$. The detection limit is defined as the sample concentration, giving signals equal to three

Table 2. Analytical performance characteristics of DLLME-FAAS for determination of silver

Parameter	Analytical feature
limit of detection / $\mu\text{g L}^{-1}$, (3σ , $n = 6$)	0.61
linear range / $\mu\text{g L}^{-1}$	0.60–120.0
r^2	0.9984
enhancement factor ^(a)	35.5
RSD / % ($20.0 \mu\text{g L}^{-1}$, $n = 6$)	1.48
sample volume / mL	10.0
sample introduction volume / μL	200.0

^(a) Enhancement factor is calculated as the ratio of slopes of the calibration graphs with and without pre-concentration.

Table 3. Results obtained for determination of Ag(I) in water samples using DLLME-FAAS

Sample	Added Ag ⁺ / μg L ⁻¹	Found / μg L ^{-1(a)}	Recovery / %
Tap water (Shahrood, Iran)	–	N.D. ^(b)	–
	8.0	7.7 (±0.2)	96.2
	20.0	19.6 (±0.5)	98.0
Tap water (Jajarm, Iran)	–	N.D. ^(b)	–
	8.0	7.9 (±0.4)	98.7
	20.0	19.2 (±0.4)	96.0
Seawater (Caspian sea, Iran)	–	N.D. ^(b)	–
	8.0	7.7 (±0.3)	96.2
	20.0	19.0 (±0.5)	95.0

^(a) Mean ± standard deviation (*n* = 3).^(b) Not detected.

times the standard deviation of blank signal, and for silver, it was 0.61 μg L⁻¹. The preconcentration factor (PF) was calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, which was 35.5. The precision of the procedure was determined as the relative standard deviations of six independent measurements of 8.0, 20.0 and 100.0 μg L⁻¹ of Ag(I) were achieved 2.53, 1.48 and 2.49 %, respectively.

Application of the Method to Real Samples

In order to evaluate the accuracy and application of the proposed method, the silver content was determined in two tap water samples (Shahrood, Iran and Jajarm, Iran), a seawater sample (Caspian seawater, Iran), and a photographic film sample. For this aim, each sample was spiked with Ag(I) and then preconcentrated and determined by the proposed procedure. In the analysis of the real samples, the standard addition technique was used, and each determination was repeated for three times. In the analysis of water samples, the contents of silver were obtained to be less than the limit of detection (Table 3). The recoveries from these samples at the spiking level of 8.0 and 20.0 μg L⁻¹ showed that the matrices of the analyzed water samples had little effect

Table 4. Results obtained for determination of Ag(I) in water samples using DLLME-FAAS

No.	Added Ag ⁺ / μg L ⁻¹	Found / μg L ^{-1(a)}	Content in the sample / mg g ⁻¹	Recovery / %
1	–	41.9	0.762	–
2	8.0	50.5 (±0.3)		107.5
3	20.0	62.1 (±0.1)		101.0

^(a) Mean ± standard deviation (*n* = 3).

on the DLLME procedure for determination of silver. The results obtained for determination of silver in the photographic film sample are given in Table 4. These results confirm good accuracy of the method. Thus the results tabulated in Tables 3 and 4 indicate the applicability of the proposed method for determination of silver in different real samples. The proposed method shows good sensitivity and precision, and has some good advantages over other methods reported in the literature. The request data for comparison of our work with some of the other researched are present in Table 5. It can be seen from these data in Table 5 that RSD and preconcentration factor (PF) of the present method are better than the other techniques. Also, LOD of this procedure is lower than the other method (except method of reference 51).

CONCLUSION

In this paper, a DLLME-FAAS method was proposed for the determination of silver in various real samples such as seawater, two tap waters, and a photographic film. DLLME is very fast compared with the other preconcentration methods. LOD of the present method is less than LOD of the most reported methods for silver(I).^{7,50,52} High recovery and good repeatability display efficiency and applicability of the method for real samples. Moreover, this method is simple, and inexpensive. The developed method was applied for the determination of silver in some real samples including sea water, top water and photographic film with satisfactory analytical results.

Table 5. Comparison of the proposed method with other reported preconcentration methods for determination of silver

Method	Sample volume / mL	Enhancement factor (or enrichment factor)	R.S.D. / %	Linear range / μg L ⁻¹	LOD / μg L ⁻¹	Reference
SPE-FAAS	50	– (10)	4.4	10.0–1000.0	3.9	[50]
SPE-FAAS	14	35 (–)	3.8	5.0–20.0	0.22	[51]
Displacement-CPE- FAAS	10	24 (–)	2.6	5.0–450.0	1.0	[52]
Ligandless-DLLME- FAAS	8	– (16)	1.5	5.0–2000.0	1.2	[7]
DLLME-FAAS	10	35.5 (–)	1.48	3.0–120.0	0.61	Present work

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