Ultra-Trace Determination of Silver in Water, Soil and Radiology Film Samples Using Dispersive Liquid-Liquid Microextraction and Microvolume UV–Vis Spectrophotometry

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ABSTRACT: *In this research, a Dispersive Liquid-Liquid MicroExtraction (DLLME) method coupled to UV-vis spectrophotometry was developed for the indirect determination of silver ion. The method is based on the catalytic effect of the silver ion on the oxidation of congo red by potassium peroxodisulphate and extraction with DLLME procedure using chloroform (extraction solvent) containing cetyltrimethyl ammonium bromide which provides counter ion and also acts as a disperser. After extraction, the phase separation is performed with a centrifugation, and the silver ion is determined in the enriched phase by UV-Vis spectrophotometry. Several factors affecting the microextraction efficiency, such as pH of the solution, extraction time, type and volume of extraction solvent were investigated. Under optimum conditions, a linear calibration graph in the range of 0.5-105.0 ng/mL of silver ion in the initial solution with $r^2 = 0.9987$ (n=10) was obtained. Detection limit of method was 0.2 ng/mL and the Relative Standard Deviation (RSD) for 3 and 70 ng/mL of silver ion was 3.5 and 1.7 (n=10), respectively. The enrichment factor was 54. The method was successfully applied to the determination of trace amounts of Ag(I) in radiology film and environmental matrices.*

KEYWORDS: *Congo red; Dispersive liquid-liquid microextraction; Ultra-trace determination; Silver.*

INTRODUCTION

Silver is one of the most important precious metals due to its application in industry and economic activity. Silver is of great interest in many fields of science and technology such as electrical industry, electronics, photos, videos and making fungicides [1]. In recent decades, silver has been used for water purification because of its antimicrobial activity. Hence silver may enter water samples [2]. The concentration of silver in environmental samples is at trace and ultra-trace levels. Moreover, the matrix interferences are serious, therefore its determination is difficult, and a preconcentration or separation method is often necessary. Several methods

have been reported for the preconcentration and separation of silver, such as coprecipitation [3, 4], Liquid-Liquid Extraction (LLE) [5], Solid-Phase Extraction (SPE) [6, 7] and Cloud Point Extraction (CPE) [8, 9] but they have some disadvantages.

In recent years, Dispersive Liquid-Liquid Microextraction (DLLME) has attracted a considerable amount of attention due to its simplicity, short analysis time, low cost, high enrichment factor and low consumption of organic solvents. In this method, an appropriate mixture of extraction and dispersive solvents is injected rapidly into an aqueous sample, resulting in the formation of a cloudy solution. The contact area between the extracting solvent and the sample solution is extremely large; thus, the extraction equilibrium is obtained rapidly. This method has been successfully applied to the concentration of various families of organic and inorganic species in water samples [10-14].

In the present study, a procedure for the Ultra-trace determination of Ag (I) using DLLME was developed. The method is based on the catalytic effect of silver ion on the oxidation of congo red by potassium peroxodisulphate. In DLLME procedure, chloroform was choice as an extraction solvent and cetyltrimethyl ammonium bromide as a disperser. The important parameters, such as reaction conditions, the type and volume of extraction solvent, and extraction time were investigated and optimized. The method was successfully used for the extraction and determination of Ag (I) in different real samples.

EXPERIMENTAL SECTION
Reagents and solutions

All chemicals were of analytical grade. The Ag (I) stock solution (1000 µg/mL) was prepared by dissolving 0.0787 g of $AgNO_3$ (Merck, Germany) in water and diluting to 50 mL in a volumetric flask. More diluted solutions were prepared daily using this stock solution. pH adjustments were performed with 0.01–1.0 mol/L HCl and NaOH solutions. A phosphate buffer solution was prepared by adding 0.2 mol/L of NaOH to 50mL of 0.2 mol/L phosphoric acid (Merck) solution and adjusting the pH to 2.3 using a pH meter.

Apparatus

A model Lambda -35spectrophotometer (Perkin Elmer) with 350 µL quartz microcells was used for absorbance measurements. To separate the phases, an ELE centrifuge (Ieccentra-CLD) was used. The pH of the solutions was controlled with a Jenway pH meter model 3520.

Dispersive liquid-liquid microextraction procedure

The extraction of the ultra-trace Ag(I) from a water sample into a microvolume of the organic solvent (chloroform) was made. 10 mL solutions containing 0.5-105.0 ng/mL of Ag(I), 2.5 mL of phosphate buffer (pH=2.3), 4.7×10^{-3} mol/L Potassium peroxodisulfate, 0.75 µg/mL 1,10 phenanthrolin and 2 µg/mL congo red were placed in a 15 mL glass tube with a conical bottom and left to stand for 5 min. Two hundred microliters of chloroform (extraction solvent) containing 0.20% (w/v) cetyltrimethyl ammonium bromide (CTAB) was injected rapidly into 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 5000 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 496 nm (against the blank). A blank solution was also run under the same procedure without adding any silver ion.

Preparation of Samples

Radiology film samples were dissolved according to the following procedure. 10 mL of concentrated nitric acid was added to 0.5 g of the film sample in a beaker and boiled for 20 minutes. The resulting solution was transferred to a 50 mL volumetric flask and diluted to the mark.

Five grams of a powdered ore sample (Dehdasht, Iran) was accurately weighed into a 50 mL glass beaker, to which 25 mL of concentrated nitric acid was added. The sample was gently heated in a sand bath at a low boiling temperature until dense white fumes disappeared. After cooling, 5 mL of 5 mol/L nitric acid and 10 mL of water were added to the beaker to dissolve the analyte. The solution was filtered into a 50 mL volumetric flask, and after washing the filter paper with water, the solution was diluted to the mark [15].

RESULTS AND DISCUSSION

The catalytic effect of the silver ion on the oxidation of congo red, Brilliant Cresyl Blue, gallocyanine and
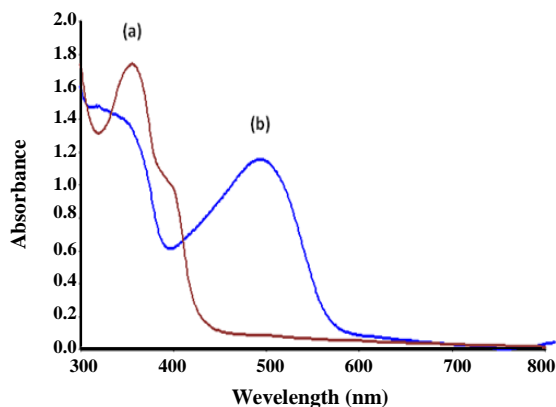
Fig. 1: UV–visible absorbance spectra of sediment phase (a) in the presence of Ag (sample) and (b) in the absence of Ag (blank).
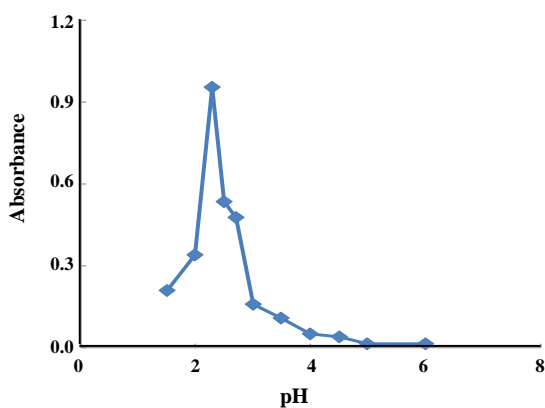

Fig. 2: Effect of pH on the determination of Ag. (DLLME conditions: Ag, 100 ng/mL; sample volume, 10.0 mL; 4.7×10^{-3} mol/L Potassium peroxodisulfate; 0.75 µg/mL 1,10 Phenanthroline; 2 µg/mL congo red; injection 200 ng/mL of chloroform (extraction solvent) containing 0.20 % (w/v) CTAB; extraction time 10 min).

azocarmine G by potassium peroxodisulphate in the presence of 1.10-Phenanthroline as an activator was examined [1, 16-18]. Congo red can be oxidized by oxidizing agents such as peroxodisulphate in acidic solution. On the other hand, the oxidation of congo red by peroxodisulphate is increased in presence of the trace amounts of silver, and 1.10-Phenanthroline as an activator [1]. Congo red is an anionic dye so cetyltrimethylammonium bromide (CTAB) was used as a cationic surfactant to form the ion pair. In order to perform the quantitative analysis spectrophotometrically,

the maximum absorption wavelength should be established. Therefore, the sample solution containing Ag was examined according to the recommended procedure of DLLME and corresponding spectra of sedimented phase were recorded in the range of 300–800 nm. As seen in Fig. 1, the maximum wavelength, 496 nm was selected to measure the decrease in absorbance.

The effect of pH

Congo red reagent is an acid-base indicator. The structural configuration and its solution absorbance depend on the pH solution. On the other hand, pH is very effective on the DLLME for different compounds. Thus, DLLME procedure for silver was carried out in the solutions with different pH values ranging from 1.0 to 6.0. As seen in Fig. 2, maximum absorption difference of the sample and the blank was at pH 2.3. Therefore, the further works for microextraction were followed at pH 2.3 by adding the 2.5 mL phosphate/phosphoric acid buffer solution.

The effect of congo red concentration

The influence of the concentration of congo red as reactant was studied ranging from 0.5 to 3.0 µg/mL. In the first method, absorption of samples containing various concentrations of Congo red (0.5-3.0) and silver 100 ng/mL were measured against chloroform (Fig. 3a). Since in low concentrations of Congo red, all Congo red was oxidized and colorless production was produced, a significant increase in absorption was not observed to 1.5 µg/mL of Congo red. At concentrations more than 1.5 µg/mL of Congo red, the Congo red was too much that the system did not have enough silver for oxidation of Congo red. So, some of Congo red, without being oxidized, entered the extraction phase. Therefore, the absorption increased. In the other method, absorption of samples containing various concentrations of Congo red (0.5-3.0) and silver 100 ng/mL were measured against the blank (a same condition with the sample without silver) (Fig. 3b). Fig. 2b shows absorption variations versus concentrations of Congo red at 1.5 µg/mL where the lines cross because there was silver before 1.5 µg/mL of Congo red. Hence, Congo red was oxidized but after that point, Congo red was not oxidized. To ensure that all the silver was used in the Congo red oxidation reaction, 2 µg/mL of Congo red was chosen as the optimum.
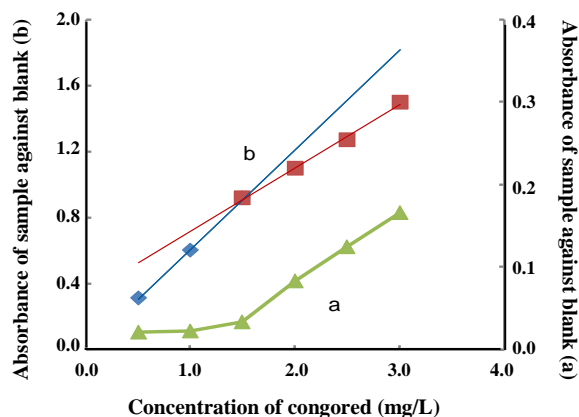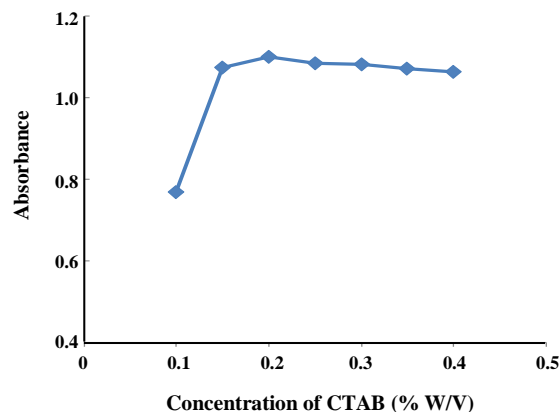
Fig. 3: Effect of congo red concentration on the determination of Ag a) absorption of samples against chloroform b) absorption of samples against blank (DLLME conditions: Ag, 100 ng/mL; sample volume, 10.0 mL; 4.7×10^{-3} mol/L Potassium peroxodisulfate; 0.75 µg/mL 1,10 phenanthroline; injection 200 ng/mL of chloroform (extraction solvent) containing 0.20 % (w/v) CTAB; extraction time 10 min).

Fig. 4: Effect of CTAB concentration of the solution on the DLLME extraction of Ag. (DLLME conditions: Ag, 100 ng/mL; sample volume, 10.0 mL; 4.7×10^{-3} mol/L Potassium peroxodisulfate; 0.75 µg/mL 1,10 phenanthroline; 2 µg/mL congo red; injection chloroform containing CTAB; extraction time 10 min).

Effect of extraction solvent and disperser

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 cetyltrimethylammonium bromide 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 consumption of volume. Therefore, chloroform was selected as the extraction solvent.

The concentration of CTAB as disperser was also an important factor for achieving good extraction performance. The influence of the CTAB concentration on the determination of Ag was evaluated in the concentration range of 0.10 to 0.40 %w/v. The results were shown that the absorbance of Ag increased with the increase of CTAB concentration up to 0.15 %w/v, and then remained constant. Thereby, CTAB concentration of 0.20 %w/v was selected for further study.

The volume of chloroform containing 0.20% (w/v) CTAB was studied between 100 to 400µL and the results are exhibited in Fig. 4. As can be seen, the absorption increased with the increase of the volume of chloroform from 100µL to 200µL, and then decreased when the volume of chloroform further increased.

The increase of absorbance with increasing of chloroform volume is due to dissolving more compounds in chloroform. But when the volume is over 200 µL, enrichment factor decreases by increasing the volume of chloroform because of increase in the sedimented phase volume. Thus, 200 µL of chloroform was used throughout this study.

Effect of extraction time and centrifugation time

The effect of extraction time (interval time between the injection of a mixture of disperser and extraction solvent before starting to centrifuge) on the performance of DLLME is considered a key factor which must be studied and evaluated. Therefore, to evaluate this parameter, different extraction times (ranging from 1 to 10 min) with constant experimental conditions were studied. 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 studied from 1 to 10 min at a rotation speed of 5,000 rpm. A centrifugation time of 5 min was selected

Table 1: Tolerance limit of foreign ions on the determination of Ag(I).

Interference	Interference/Ag Ratio
Cl^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, Li^+, Na^+, K^+, Al^{3+}	1000
Mn^{2+}, ClO_4^-, PO_4^{3-}	800
Ca^{2+}, Mg^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}	200
Hg^{2+}, Zn^{2+}, Cu^{2+}, CN^-	10

Table 2: Determination of silver in real samples.

Sample	Added silver (ng/mL)	Founded[a] silver (ng/mL)	Recovery (%)
Tap water	0	N.D[b]	-
	70	65.2±0.5	93.2
	100	94.6±0.7	94.6
River water 1	0	N.D	-
	70	68.0±0.5	97.2
	100	96.9±0.8	96.9
River water 2	0	ND	-
	70	68.9±0.6	98.4
	100	98.5±0.8	98.5
Soil	0	ND	-
	70	69.4±0.6	99.2
	100	98.1±0.8	98.2
Radiology film	0	21.5±0.3	-
	30	52.1±0.4	101.1
	70	87.6±0.5	95.7

a) Mean ± standard deviation(n=4), b) Not detected.

as the optimum, since complete separation occurred during this time and no appreciable improvements were observed for a longer interval.

Interference studies

The effect of diverse cations and anions on the determination of 100 ng/mL Ag (I) by the proposed method was studied. Each ion was considered to be interference when it caused an error greater than ±5% in the determination of silver. As shown in Table 1 the proposed method was relatively selective for Ag (I).

Analytical figures of merit

A linear calibration curve was obtained in the range of 0.5-105.5 ng/mL of Ag (I) in the initial solution. The limit of detection (LOD) of the proposed method based on three times the standard deviation (3Sb) and for 10 replicated measurements of the blank solution at optimized conditions was 0.2 ng/mL. The relative standard deviations (RSD) for the determination of 3 and 70 ng/mL of Ag (I) were 3.5 and 1.7% (n=10), respectively. The enrichment factor for the suggested DLLME method is calculated by the ratio of the slope of the calibration curve and preconcentration curve. Thus, an enrichment factor of about 54 was achieved by using this procedure.

Application to real samples

To demonstrate the performance and validation of the present method, the Ag was determined in water, soil and radiology film samples. The tested water samples were found to be free from Ag according to the optimized procedure. The recovery tests were performed by the analysis of the samples spiked with known amounts of Ag(I). The analytical data of this investigation are given in Table 2. As can be seen, the Ag(I) recovery for the spiked samples is quantitative.

Table 3: Comparison of the proposed method with some of the previously reported methods for the determination of silver(I).

Number	Methods/Reagent(s) used	Detection limit	Real sample	References
1	Solid phase extraction	4 ng/mL	Drinking water	19
2	Ionic sensor	0.5×10^{-6} mol/L	Aqueous media	20
3	Tween 20-stabilized AuNPs	0.1×10^{-6} mol/L	Drinking water	21
4	2-ME/Au NPs	70×10^{-9} mol/L	-	22
5	2MNA-AuNPs	25×10^{-9} mol/L	Water solution	23
6	cationic polymerdirected AuNPs	48.6×10^{-9} mol/L	Water solution	24
7	benzo-15-crown-5/	12.5×10^{-9} mol/L	AuNPs lake and drinking water	25
8	kinetic method	0.125 ng/mL	-	26
9	DLLME	30 ng/mL	Nano silver and semiconductor thin films	27
10	DLLME	0.41 ng/mL	Water, radiology film processing wastewater and ore samples.	28
11	DLLME	2.1×10^{-9} mol/L (0.2 ng/mL)	Tap water, river waters, soil, and radiology film	Present work

CONCLUSIONS

In the present study, a dispersive liquid–liquid microextraction method was employed for the sensitive determination of silver. The present approach can be used for the determination of silver in the range of 0.5-105.0 ng/mL with a limit of detection 0.2 ng/mL (2.13×10^{-9} mol/L). Miniaturization of toxic organic solvent using DLLME combined with microvolume UV–Vis spectrophotometry allows the development of a green method which is environment-friendly. Besides, the simplicity of operation, rapidity, low sample volume, low cost and high preconcentration factor are some advantages of the suggested method. A comparison between presented approach and previously reported a method for the determination of Ag is given in Table 3. As can be seen in the table, the LOD of suggested method is better or comparable to the reported techniques. The method was applied successfully for different samples and this is an important advantage.

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