

Ultra-Trace Silver Determination in Biological and Water Samples by Electrothermal Atomic Absorption Spectrometry after Electrodeposition on a Graphite Probe

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A rapid and simple procedure was developed for selective and sensitive determination of ultra-trace silver in biological and environmental samples using the electrodeposition on a graphite probe modified with palladium followed by electrothermal atomic absorption spectrometry. Several experimental parameters for the electrodeposition, such as deposition potential, electrolyte concentration, pH of solution and deposition time were optimized. The calibration graph after preconcentration was linear in the range of 10–250 ngL⁻¹ with correlation coefficient of 0.9989 under the optimum conditions for procedure. The limits of detection (LOD) and quantification (LOQ) based on (3 σ) and (10 σ) were 2.8 ngL⁻¹ and 9.4 ngL⁻¹ respectively. Related standard deviation (RSD) for eight replicate measurements of 100 ngL⁻¹ silver was 4.3%. Samples were digested completely in a closed microwave digestion system using only perchloric acid, and interference owing to various cations was also investigated. The proposed procedure was successfully applied to determine silver in blood, urine and some environmental samples with satisfactory analytical results.

Keywords: Silver; Palladium; Electrodeposition; Preconcentration; Microwave digestion; Electrothermal atomic absorption spectrometry.

INTRODUCTION

Silver is one of the commercially and industrially important elements. The widespread use of silver compounds in industry, medicine, jewelry, cloud seeding and electrical instruments has resulted in an increasing silver content of environmental and biological samples. Because of its antibacterial properties, silver compounds are often used extensively to disinfect water used for drinking and recreation. On the other hand, novel investigations on the interaction of silver with vital nutrients, especially selenium, copper, vitamins E and B12 have been performed to reveal its potential toxicity.^{1–6} Hence, a simple, sensitive and powerful method is necessary to determine silver at trace and ultra-trace levels. The direct determination of silver in complex matrix by common methods, such as flame atomic absorption spectrometry (FAAS),⁷ electrothermal atomic absorption spectrometry (ETAAS),⁸ neutron activation analysis (NAA),⁹ inductively coupled plasma atomic emission spectrometry (ICP-AES),¹⁰ is usually difficult because of low concentration of silver and matrix interference and an initial sample pretreatment is necessary. Several different methods, such as liquid-liquid extraction (LLE),¹¹ cloud point extraction (CPE),¹² and solid phase extraction (SPE),^{13,14} have been used for this purpose. Electrodeposi-

tion coupled with electrothermal atomic absorption spectrometry has been demonstrated to be a powerful method to attain sensitive and selective determination of ultra-trace analysis in a complex matrix.¹⁵ This combined technique has ability to discriminate among very labile, moderated labile and inert metal species. This advantage is very important for determining toxicity levels of different species of elements. In this technique, electrolytic preconcentration is done by plating the metals on a pyrolytic graphite platform,¹⁶ high melting-point metal wires¹⁷ or a tubular pyrolytic graphite coated furnace,¹⁸ used as an electrode. In some of these arrangements, flow systems have been designed.¹⁹ After electrodeposition, analyte should be dissolved from the electrode in a small volume of acid and the whole volume of eluent was injected into the graphite tube atomizer.²⁰ Matousek et al. have introduced the in-situ electrodeposition-ETAAS technique.²¹ Another approach utilizes the electrodeposition of analyte from a larger volume of sample onto the graphite electrode in the form of a disc²² and, recently, a probe.²³ These graphite parts were directly inserted into the graphite tube atomizer. The aim of the present work is to design an electrodeposition system for preconcentration and separation of ultra-trace amount of silver. The graphite probe was modified with electro-

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chemically deposited Pd and existence of palladium in the graphite surface was observed by the scanning electronic microscope (SEM). The procedure was successfully applied for the determination of silver in whole blood, urine, rice and water samples.

EXPERIMENTAL

Apparatus

A GBC (GBC Scientific Equipment, Australia) double beam, Model 932 plus, atomic absorption spectrometer equipped with a GF-3000 graphite furnace atomizer and a PAL-3000 auto-sampler controlled by the AVANTA 1.33 software were used for the determination of silver. Deuterium lamp background correction was employed to correct non-specific absorbance. A mono-atomic silver hollow cathode lamp (GBC Scientific Equipment, Australia) was used as the radiation source. The operating conditions of a silver hollow cathode lamp were those recommended by the manufacturer. Pyrolytically coated graphite tubes were used throughout. Measurements were performed in the peak areas mode. The detailed graphite furnace conditions used for the determination of silver is shown in Table 1. Controlled potential electrodeposition was made with a potentiostat/galvanostat AUTOLAB (EcoChemie, The Netherlands) model PGSTAT 30 controlled by the GPES 4.9 software (EcoChemie). A three-electrode cell containing a graphite probe as a working electrode, a Pt wire (Azar electrode Co., Iran) as a counter electrode and Ag/AgCl (Metrohm, Zurich, Switzerland) as a reference electrode were used. Dissolved oxygen was removed from solutions by purging nitrogen (99.999%) (Roham gas Co., Tehran, Iran) for at least 10 min prior to each electrodeposition. All solutions were mixed by an adjustable magnetic stirrer during each deposition step. A scanning electron microscope (SEM) model S-4160 (Hitachi, Japan) was used for graphite surface image analysis. A Multiwave 3000 microwave sample preparation system (Anton Paar, Graz, Austria) was used in this study. The graphite probe was prepared from graphite rod (2 mm, Azar electrode Co., Iran) and the final rod was turned to a 0.9 mm thickness, ground by a fine emery paper and polished by a dense filter paper. The ultimate thickness of the probe was 0.7 mm.

Reagents and solutions

All the reagents were prepared from the analytical reagent grade chemicals. De-ionized water obtained from a Milli Q-water purification system (Millipore, Bedford, MA, USA) was used for preparing all solutions. Analytical grade of acids, bases, salts and other chemicals used in this study was obtained from Merck (Darmstadt, Germany). Before being used, laboratory glassware and pipettes for ultra-trace analysis were kept in 10% (v/v) nitric

Table 1. Instrumental parameters and temperature program for silver analysis

Wavelength (nm)	328.1			
Lamp current (mA)	4			
Slit width (nm)	0.5			
Measurement mode	Peak Area			
Background correction	Deuterium			
Graphite furnace temperature program				
Heating step	Temperature, °C	Time, s		Ar gas flow rate, L min ⁻¹
		Ramp	Hold	
Drying	120	15	10	0.5
Pyrolysis	450	10	5	0.5
Atomization	2000	1	2	0
Cleaning	2200	1	5	0.5

acid aqueous solution overnight, followed by ultra-sonication for 1 h and finally rinsed three times with deionized water. Silver work solutions were prepared daily by appropriate dilution of a standard silver solution (Darmstadt, Germany). In this study, all the real samples were obtained from Esfahan, Iran.

Sample preparation

Water samples: For water samples, little sample preparation was required. Samples were collected in an acid-washed polyethylene bottle and brought to the laboratory. Upon arrival at the laboratory, an aliquot of the water sample was filtered through a 0.45 μm membrane filter and stored in an acid-washed plastic bottle. At all stages, during the sample collection procedure care was taken to avoid sample contamination. Prior to the analysis, sufficient perchloric acid (70% v/v) was added to the samples until the acid concentration reached 0.6 M.

Rice, urine and blood samples: 1.00 g of powdered rice was accurately weighed by a microanalytical balance and transferred into a tetrafluoromethaxil (TFM) vessel, to be processed with 5 mL of HClO₄ 70% in the microwave digestion system. For urine or blood samples, 5 mL was mixed with 1 mL of perchloric acid 70% into a TFM vessel. Microwave digestion was done according to the following program: step 1 (time: 2 min, power: 250 w), step 2 (time: 2 min, power: 0 w), step 3 (time: 6 min, power: 250 w), step 4 (time: 5 min, power: 400 w), and step 5 (time: 5 min, power: 600 w). After complete digestion, acquired solutions were heated to reduce perchloric acid concentration as possible as, and then digested solutions were transferred to volumetric flasks and diluted with 0.6 M perchloric acid up to 25 mL.

Modification of the graphite probe surface

The graphite probe was firmly sealed with a Teflon band, except for the end part (2 mm) in which the metal was deposited. 50 mL of solution containing 3×10^6 ngL⁻¹ Pd in HCl 1% was put

in a polyethylene vessel stirred with an electromagnetic stirrer and the galvanostatic electrolysis was performed. The electro-deposition of Pd on the graphite surface was carried out in two steps. In the first step, a current of 2 mA for 30 min and then immediately a 10 mA for the next 30 min were applied. For removing possible silver contamination from the electrolyte, the unwrapped probe was inserted into a graphite tube and the heating program was applied as described in Table 1. A new Pd-modified probe was conditioned by processing 10 heating cycles according to the conditions in Table 1.

Electrodeposition of silver and AAS determination

The Pd-modified, purified and conditioned graphite probe was tightly sealed with Teflon and dipped into 25 mL of water samples, blood, urine or rice in a polyethylene vessel. The sample solution was stirred at 300 rounds per minute (rpm) by a magnetic stirrer, and -0.4 V potential (vs. Ag/AgCl) was applied. Based on the required sensitivity, potentiostatic electrodeposition took between 0.5 to 5 min. After electrolysis, the Teflon strip was detached and the part with deposited analyte was rinsed with a small volume of double distilled water to diminish the amount of adhered matrix salt and dried at ambient temperature. Afterward, the probe was inserted into the graphite atomizer and the heating program was started according to the conditions in Table 1.

RESULTS AND DISCUSSION

Optimization of the effective parameters on the deposition

A good efficiency of electrodeposition influenced by several factors such as nature of substrates, supporting electrolyte, deposition potential, time of deposition and stirrer speed, was achieved. The optimum conditions for efficient and rapid electrodeposition of silver were investigated by 25 mL of 100 ngL^{-1} standard solution. Each test was repeated three times and results were presented as the mean of repeated measurements.

Deposition potential

One of the important parameters in the electrodeposition procedure is potential applied to the working electrode.²⁴ This parameter drastically influenced the yield of deposition, so it was necessary to optimize the potential. When potential was convenient and adequate, a reasonable deposition yield was obtained. However, the more the negative potential was applied, the greater the possibility of hydrogen evolution occurred. Hydrogen evolution on the cathode electrode surface led to deposition yield deduction and somewhat unstable precipitation of metal on the electrode surface, which would probably waste by rinsing the

electrode. In the presented work, electrodeposition was done under controlled cathode potential. In order to reach optimum condition, potential was applied between (-0.1 to -0.8) V, and absorption of silver was measured for each potential. The results showed that absorption increased with the increase of potential just around -0.4 V and then deposition yield and absorption decrease. At first point of view, it seems that hydrogen evolution contributes to increase deposition yield because the solution is mixed by moving the hydrogen bubbles which decreases thickness of diffusion layer, so the ions can transport to the electrode surface easily. On the other hand, these bubbles cause the available surface area for ions resulting in reduction prevention. The variation of the absorption signal versus deposition potential curve is shown in Fig. 1. As can be seen, the curve has a maximum in the -0.4 V.

Supporting electrolyte

The yield of silver electrodeposition was affected by type and concentration of supporting electrolytes. For that reason, five types of electrolytes, H_2SO_4 , HCl, CH_3COOH , HNO_3 and HClO_4 were selected so that their ionic strength, as a proper supporting electrolyte in the electrodeposition step, was investigated. HClO_4 revealed higher performance than other electrolytes. The effect of different HClO_4 concentrations from 0.2 to 1 M on the absorption signal is shown in Fig. 2. As can be seen, the maximum absorption was achieved at 0.6 M. therefore, 0.6 M was chosen as optimum concentration of HClO_4 . Possibly, increasing the absorption signal in the high concentrations of HClO_4 was due to complete analyte releasing.

Time of deposition

Another important factor that controls efficiency of

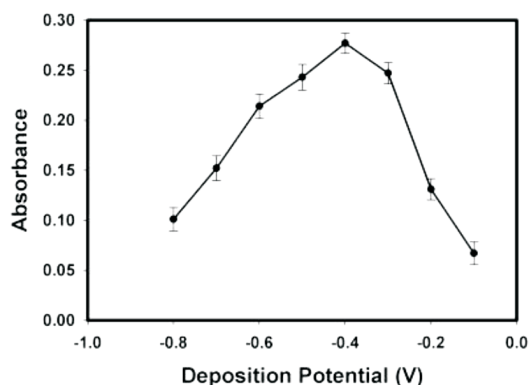


Fig. 1. Plot of silver absorbance signal versus deposition potential for 1 min electrodeposition from 25 mL solution containing 100 ngL^{-1} Ag in 1 M, HClO_4 .

the deposition is the time of the deposition. Also, the sensitivity of the method can be increased by enhancing the deposition time. The dependence of the absorbance signal for electrodeposited silver to the time of the deposition is shown in Fig. 3. As can be seen, in first 30 seconds there is a strongly dependence between the absorption signal and deposition time. In first 30 seconds, silver deposit on activated graphite surface and after that probe surface is saturated by silver and second layer of silver is deposited on first layer. By increasing time of deposition, total time of experiment raises and, as it can be seen in Table 4, when deposition time increases, RSD of the method raises and R^2 declines. Therefore, we selected 1 min for electrodeposition time.

Stirrer speed

The yield of the deposition depended on the rate of mass transport to the surface electrode during the electro-

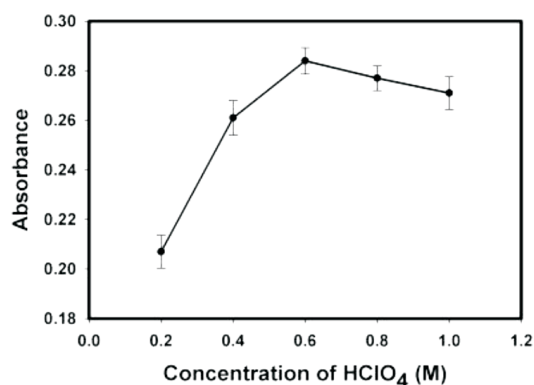


Fig. 2. The effect of different concentration of HClO_4 on silver absorbance signal for 1 min electrodeposition at -0.4 V, from 25 mL solution containing 100 ngL^{-1} Ag.

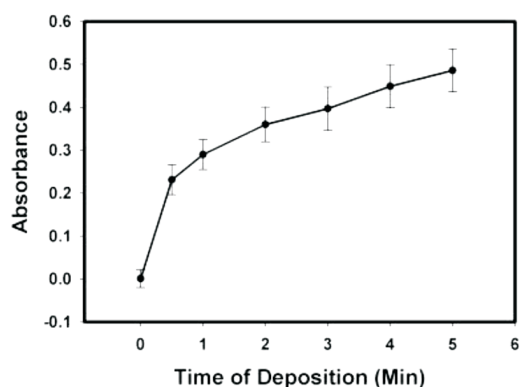


Fig. 3. Dependence of the silver absorbance signal on the time of electrodeposition at -0.4 V, from 25 mL solution containing 100 ngL^{-1} Ag in 0.6 M, HClO_4 .

deposition, and this rate was affected by the stirring speed of solution. To obtain the optimum mixing speed by a magnetic stirrer, the solution was stirred at different speeds and absorption signal was measured. The maximum absorption was achieved at 300 rpm, and significant absorption changes did not appear under 300 rpm. Therefore, 300 rpm was selected as the stirrer speed.

Optimization of temperature program for ETAAS

Selection of an appropriate pyrolysis temperature is very important to remove the matrix as much as possible and to prevent pyrolysis loss of the analytes prior to atomization. Fig. 4. shows the effect of pyrolysis temperature on the absorbance, in the range of $300\text{--}600$ °C. As can be seen, the maximum absorbance was achieved at 450 °C in the presence of chemical modifier. It is noteworthy to mention that the chemical modifier increases the thermal stability of silver. However, when the pyrolysis temperature was over 500 °C, the signal of analyte decreased rapidly as the pyrolysis temperature increased. Therefore, 450 °C was selected as the optimized pyrolysis temperature for the silver determination. The effect of the atomization temperature, in the range of $1,700\text{--}2,400$ °C, on the analytical signal of silver was also studied using a pyrolysis temperature of 450 °C. The results are shown in Fig. 4. In the presence of chemical modifier, the maximum signal was obtained at about $2,000$ °C. Therefore the atomization temperature of $2,000$ °C was selected for the further experiments. The experimental results showed that atomization time had little effect on the atomic signal of silver. Therefore, an atomization time of 2 s was selected. The partly high pyrolysis and atomization temperatures for silver used in this work were due to the fact that the silver atomized at solid form.

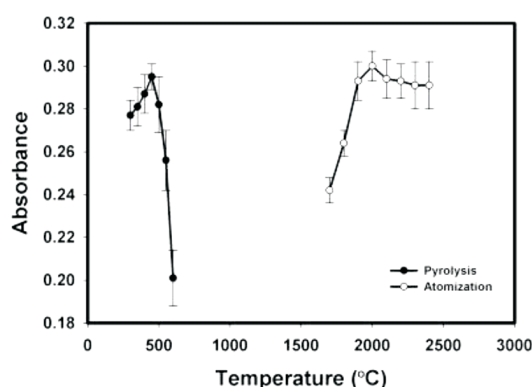


Fig. 4. Pyrolysis curve (●) and atomization curve (○) for 1 min electrodeposition at -0.4 V, from 25 mL solution containing 100 ngL^{-1} Ag in 0.6 M, HClO_4 .

Palladium modification study

It has been observed that samples containing high concentration of acids and chloride led to the deterioration of the graphite surface. In order to prevent this, impregnation with a solution of noble metal salts was applied.²¹ For this purpose, many researchers have used the electrochemical deposition of Pd method introduced by Matousek and Powell.²⁰ It is confirmed that the electrodeposited Pd used for modification purposes is distributed over the graphite surface in the form of globular islands. The migration of palladium within the sub-surface part of the graphite and the formation of intercalation compounds with carbon play a significant role in the permanent performance of the modification.^{25,26} This procedure has some advantages: for instance, the reservoir of noble metals in the sub-surface is available for several hundreds of heating cycles contributing to save reagents and analysis time. Also, Pd coating shielded the active sites to reduce the carbon-analyte interaction and prevented carbide formation. In this work, there were numerous pores on graphite structure which lead to silver diffusion into the pores of the graphite. During atomization step, diffused silver was atomized later than those deposit on surface and produced absorption peak with delay. Besides, since all existence silver in pores did not at-

omize during one atomization step, they led to memory effect on next measurements. As it can be seen in Fig. 5 (a) and (b), after graphite probe surface modification with Pd, mentioned problem was solved and absorption peak appeared in one step. When the probe was immersed in a solution containing $100 \text{ ng L}^{-1} \text{ Ag}$ for 60 s, it was observed that a signal of 0.05 was obtained after the probe was rinsed, even when no potential was applied and the probe was known to be free from silver contamination. This was possibly due to the diffusion of the silver into the pores of the graphite. By electrodeposition Pd to modify surface, the probe gave no measurable absorbance after being immersed in the silver solution. The long-term performance of the modifier was tested in detail for palladium. Based on the experiments, average $29 \text{ } \mu\text{g}$ of Pd was deposited on the graphite probe during 30 min at 2 mA and the next 30 min at 10 mA. With an atomization temperature of $2,000 \text{ } ^\circ\text{C}$, 340 atomization cycles were performed without significant losses of silver during thermal stabilization, but after about 350 firings, Pd should be deposited again. Only one probe was used without significant losses of RSD during throughout the work. In order to achieve an estimated Pd density on the surface, the amount of palladium in solution was calculated before and after electrodeposition. The concentration of Pd was determined by ETAAS with direct injection into a graphite tube. In this work, an average surface density of $6.2 \text{ } \mu\text{g mm}^{-2}$ was calculated for Pd. Similar Pd density ($1.2 \text{ } \mu\text{g mm}^{-2}$) was reported by other investigation.²³ The SEM images of the surface of graphite modified with palladium in two different magnitude are shown in Fig. 6 (a) and 6 (b).

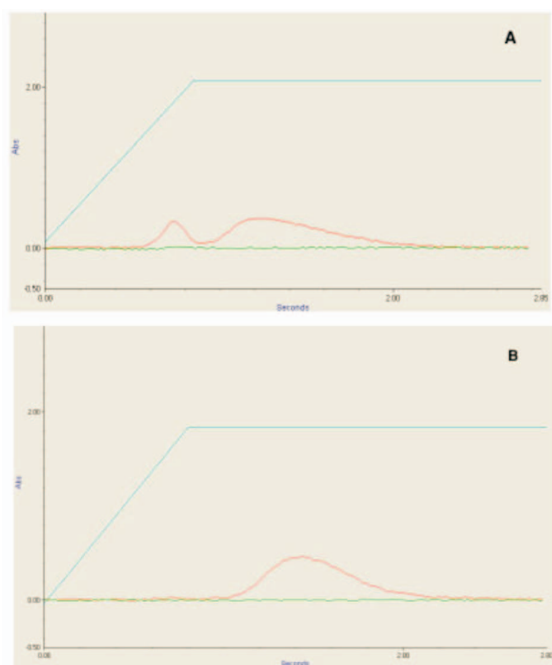


Fig. 5. The atomization signal of silver after electro-deposition on probe at -0.4 V , from 25 mL solution containing $100 \text{ ng L}^{-1} \text{ Ag}$ in 0.6 M , HClO_4 . Before (A) and after (B) modification with Pd.

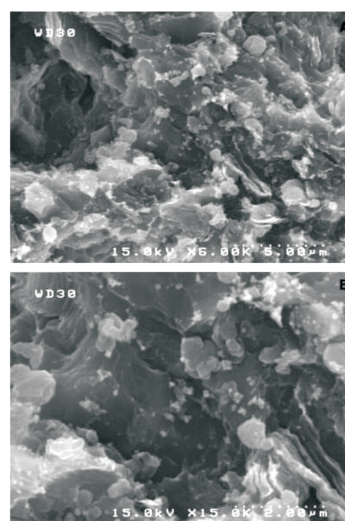


Fig. 6. The SEM images of the graphite probe surface modified with Pd. (A) $6000 \times$ and (B) $15000 \times$.

Table 2. Determination of silver in real samples

Samples	Added, ngL ⁻¹	Found, ngL ⁻¹ (n = 3) ± sd	Recovery, %
WB ^a	-----	80 ± 4	-----
Urine ^a	-----	ND ^b	-----
Water ^c	-----	69 ± 3	-----
Water ^d	-----	197 ± 6	-----
Water ^e	-----	209 ± 7	-----
Rice ^{f,g}	-----	59 ± 3	-----
	-----	257 ± 8	99
	Certified value (μg L ⁻¹)	Found value (μg L ⁻¹) ^h	
Water (NIST-SRM1643e)	1.06 ± 0.043	1.10 ± 0.053	103

^a Whole blood and urine of multiple sclerosis patients, Esfahan, IRAN.

^b Not detected.

^c Drinking water, Esfahan, IRAN.

^d Mineral water, Esfahan, IRAN.

^e River water, Zayandeh rood, Esfahan, IRAN.

^f Rice, Falavarjan, Esfahan, IRAN.

^g nanogram per gram (ng gr⁻¹)

^h (Mean ± σ, n = 3, P = 0.95)

As can be seen, white spots of Pd on graphite surface are completely recognizable.

Determination of silver in real samples

The proposed methodology was successfully applied to determination of silver in several biological and environmental samples. Recovery experiments were carried out by spiking the samples with different amounts of silver before any pretreatment and the percentage recoveries were calculated. Table 2, shows the obtained results. The recovery values calculated for the added standards were always higher than 95%, thus confirming the accuracy of the procedure and its independence from the matrix effects. In order to validate the developed method, it was applied to determine silver in standard reference materials of water (NIST-SRM1643e), and the analytical results are given in Table 2. As can be seen, analytical results were in good agreement with the certified values, and no significant differences have been observed.

Interferences study

The selectivity of the method was evaluated by adding different amounts of potentially interfering species.

Table 3. Effect of interfering ions in the determination of Ag (100 ng L⁻¹) under the optimum experimental conditions

Coexisting ion	Added as	Concentration of coexisting ion × 10 ⁶ (ng L ⁻¹)	Recovery of silver ion, %
Pb ²⁺	Pb(NO ₃) ₂	5	98
Cd ²⁺	Cd(NO ₃) ₂	5	97
Co ²⁺	CoSO ₄	10	99
Ni ²⁺	NiSO ₄	10	99
Mn ²⁺	MnSO ₄	10	96
Fe ²⁺	FeSO ₄	10	99
Bi ³⁺	Bi(NO ₃) ₃	10	101
Zn ²⁺	ZnSO ₄	5	99
Cu ²⁺	CuSO ₄	10	100
Mg ²⁺	MgCl ₂	500	100
K ⁺	KCl	500	101
Na ⁺	NaCl	500	100

Different amounts of ions were added to the test solution containing 100 ngL⁻¹ of silver and then operated as described method under optimization parameters. An ion was considered to interfere when its presence produced a variation of more than 5% in the absorbance of the sample. For errors smaller than 5%, the permitted quantity of each coexisting ion is given in Table 3. Owing to the electrodeposition step, there was no interference from ions when silver is determined by the present method. These results allow us to apply the suggested system for interference-free determination of ultra-trace silver in biological and environmental samples.

Calibration and analytical performance

For the present procedure, the analytical characteristics data are shown in Table 4. Sensitivity was calculated from the mean of the slope of the calibration graph, as defined by IUPAC.²⁷ Three and ten times the standard deviation of blank values were used in the LOD and LOQ calculations, respectively. The results showed a noticeable improvement in LOD in comparison with ETAAS. This was attributed to an improvement in the analyte signal due to the preconcentration step. This technique also showed an enhancement in the slope of the calibration curves in the measurement of silver due to the analyte being separated by deposition on the probe surface from the interfering matrix. Under the optimum conditions, the related standard deviation (RSD) 4.3% was obtained for eight replicate measurements of 100 ngL⁻¹ silver. Characteristics data of the present method at 1 and 3 min electrodeposition with direct injection for silver determination are compared in Table 4.

Table 4. Analytical characteristics of the proposed method

Analytical characteristic	Direct injection ^a	ED-ETAAS ^b	
		1 min	3 min
Linear Range, ngL ⁻¹	500-12000	10-250	10-250
Correlation coefficient	0.9989	0.9989	0.9984
Slope	0.051	2.702	3.515
BEC ^c , ngL ⁻¹	110	1.8	1.6
R.S.D, % (n = 8)	2.6	4.3	4.4
LOD, ngL ⁻¹	140	2.8	2.1
LOQ, ngL ⁻¹	380	9.4	7.2

^a Direct injection of a 20 μ L sample solution^b Electrodeposition-Electrothermal Atomic Absorption Spectrometry^c Background equivalent concentration

CONCLUSIONS

Results presented in this work demonstrate an effective approach to improve the detection limit of ETAAS for silver determination. This procedure is very selective and shows high tolerance to interferences from complex matrix due to electrodeposition step. Also, the proposed method is easy, safe, rapid and inexpensive for preconcentration and separation of ultra-trace silver and determination by ETAAS in environmental and biological samples.

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