

Voltammetric Determination of Silver with a New Multi-Walled Carbon Nanotube Modified Paste Electrode¹

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Abstract—This study introduces the sensitive determination of silver using modified carbon paste electrode based on multi-walled carbon nanotubes and a new synthesized chelating agent of N-(4-{4-[(anilino-carbothi-oyl)amino]benzyl}phenyl)-N-phenylthiourea. This electrochemical method is based on accumulation of silver ions at the surface of a new multi-walled carbon nanotube modified paste electrode. After preconcentration, the measurements were carried out in a closed circuit by electrolysis of the accumulated Ag(I) ions by voltammetric scanning from -0.2 to $+0.2$ V. Under the optimized conditions, a linear response range from 0.5 to 270 ng mL⁻¹ was obtained. The detection limit and relative standard deviation for seven replicate measurements were 0.079 ng mL⁻¹ and $\pm 2.4\%$, respectively. The procedure was applied to determination of silver(I) in water, tea leaves and a certified reference material with satisfactory results.

Keywords: anodic stripping voltammetry, carbon paste electrode, silver, N-(4-{4-[(anilino-carbothi-oyl)amino]benzyl}phenyl)-N-phenylthiourea, carbon nanotube

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1. INTRODUCTION

Silver has been extensively used in different applications such as catalysis, electronics, photonics and photography. For example, silver has the highest electrical and thermal conductivity and reflectivity of all metals. Silver exists in nature in the form of silver sulphide minerals or coexists with other non-ferrous metal sulfide ores [1].

It is reported that the concentration of silver in water higher than 1.6 nmol L⁻¹ is toxic to fish and microorganisms. It has also been found that silver is toxic to humans at a concentration as high as 0.9 μ mol L⁻¹ in drinking water [2]. Thus, the determination of trace amounts of silver ions in various media is necessary. Some effective analysis methods to determination of silver ions such as synchronous fluorescence spectrometry (SFS) [3], spectrophotometry [4], flame atomic absorption spectrometry (FAAS) [5], electrothermal atomic absorption spectrometry [6] and electrochemical methods [7] have been reported.

Among different electrochemical techniques, stripping voltammetry (SV) plays an important role and has been recognized as one of the most powerful tools in trace and ultra-trace analysis of heavy metals

and some organic compounds [8, 9], due to its unique preconcentration capability in conjunction with different electrode materials. One of the most popular and common electrodes can be applied in electrochemical methods is carbon paste electrode (CPE) [10].

Carbon paste electrodes have attracted attention as ion selective electrodes mainly due to their advantages such as simple preparation and operation, reusability, low cost, stable response and applicability for the determination of various compounds. Moreover, CPEs belong to nontoxic and environmentally friendly electrodes. Due to the above mentioned properties, carbon paste electrode seems to be especially promising. To our knowledge, there are some reports on determination of metal ions and biological compounds using carbon paste electrodes [8, 11, 12].

The aim of the present investigation is to develop a new CPE, modified with N-(4-{4-[(anilino-carbothi-oyl)amino]benzyl}phenyl)-N-phenylthiourea (ACABP) as a new chelating agent (Fig. 1) and multi-walled carbon nanotubes (MWCNTs) for the selective preconcentration and determination of Ag(I) ions by differential pulse anodic stripping voltammetry (DPASV). The effects of different parameters such as electrode composition, stripping medium, accumulation time and reduction potential have been evaluated and optimized. The method has also been extended to the

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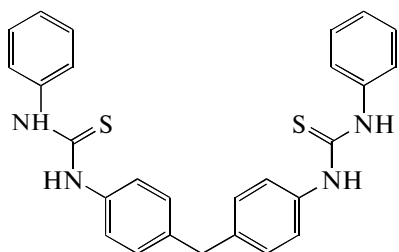


Fig. 1. N-(4-{4-[(anilinothioyl)amino]benzyl}phenyl)-N-phenylthiourea (ACABP) structure.

determination of the silver amount in the presence of a large amount of other ions and from some real samples with satisfactory results.

2. EXPERIMENTAL

2.1. Materials and Reagents

Highly pure graphite powder and MWCNTs with 3–20 nm diameters, core diameter: 1–10 nm, SBET: 350 m² g⁻¹ and 95% purity were purchased from Merck (Darmstadt, Germany). Silver nitrate (AgNO₃) (Merck, Darmstadt, Germany) solutions were prepared in deionized water and their concentrations were checked by an atomic absorption spectrometer (PerkinElmer model 2380). The silver solutions were placed in the dark and protected against light in amber bottles. The chelating agent, N-(4-{4-[(anilinothioyl)amino]benzyl}phenyl)-N-phenylthiourea was synthesized and purified as described elsewhere [13]. HCl, HF, HNO₃, CH₃COOH, H₂SO₄ and H₃PO₄ were purchased from Merck (Darmstadt, Germany). Also high pure nitrogen was used for deaeration and deionized water was used throughout.

2.2. Apparatus

Voltammetric experiments were performed using a Metrohm electroanalyzer (Model 757 VA Computrace). The measurements were recorded using VA Computrace version 2.0 (Metrohm, Herisau, Switzerland) run under the Windows 98 operating system. All voltammograms were recorded with a three electrode system consisting of an Ag/AgCl electrode as the reference electrode, a platinum wire as the auxiliary electrode and the CPEs (modified or unmodified) as the working electrode. All the electrochemical experiments were carried out under pure nitrogen atmosphere at room temperature.

2.3. Sample Preparation

2.3.1. Water samples. Three water samples, including; tap water (Kerman drinking water, Kerman, Iran), well water (Shahid Bahonar University of Kerman, Kerman, Iran) and wastewater (Iron Factory,

Bafgh, Yazd, Iran) were selected. These samples were filtered to remove suspended particulate matters, stored at 4°C in a refrigerator and the suggested method was applied for the determination of silver content.

2.3.2. Tea leaves. Tea leaves were immersed in acetone for 30 min, washed with water and then dried. 1.5 g of sample was weighed accurately, digested by 30.0 mL of a mixture solution of HClO₄ and HNO₃ (1 : 8, v/v) at low temperature. The digested solution was dried under elevated temperature and then several drops of H₂SO₄ (1 : 1, v/v) were added to the residue. After leaching with water, the residue was transferred to a 100.0 mL measuring flask, diluted to the mark with deionized water [14], an aliquot of the solution was selected and the experiment was carried out according to the procedure mentioned earlier.

2.3.3. Certified reference material. In order to confirm the validity of the developed procedure, this method has also been applied for the determination of silver content in a Certified Reference Material; MA-1b reference gold ore.

A 250.0 mg sample (MA-1b reference gold ore) was taken and dissolved completely in a mixture of HNO₃, HCl and HF (2 : 4 : 1 volume ratio) with heating. The solution was cooled, diluted and filtered [14]. The volume of the filtrate was raised to 100.0 mL with deionized water in a volumetric flask, an aliquot of the sample solution was taken individually, and the silver content was determined by the recommended procedure.

2.4. Modified and Unmodified Electrode Preparation

The unmodified carbon paste was prepared by hand mixing of 70 mg of reagent-grade graphite powder and 30 μL of silicon oil with a mortar and pestle. The modified carbon paste was prepared by mixing of 60 mg of high purity graphite powder, 30 μL of silicon oil, 5 mg of chelating agent and 5 mg of nanotube (for increasing the current and sensitivity) and following hand mixing in a mortar and pestle. A fresh electrode surface was obtained by squeezing out a small amount of paste into the end of a glass tube (ca. 3.0 mm i.d. and 10 cm long), scrapping off the excess against a conventional paper and polishing the electrode on a smooth paper to obtain a shiny appearance. The electrical connection was made with a copper wire.

2.5. Accumulation and Voltammetric Procedures

The method is based on a closed circuit accumulation of silver ions at the surface of ACABP-MCPE. The analysis of Ag(I) ions using differential pulse anodic stripping voltammetry was carried out using the following steps: For preconcentration step, the ACABP-MCPE was immersed in a stirred 25.0 mL of HCl (0.2 mol L⁻¹) containing a known amount of Ag(I) for 5 min where the Ag(I) ions were accumulated

and reduced at the surface of the electrode in -0.9 V. Finally the differential pulse voltammograms were recorded by scanning from -0.2 to $+0.2$ V (with 30 mV s^{-1} scan rate, 100 mV pulse amplitude and 4 ms pulse period). All the measurements were carried out at room temperature ($\sim 23 \pm 1^\circ\text{C}$).

3. RESULTS AND DISCUSSION

3.1. Voltammetric Behavior of Silver(I) at ACABP-MCPE

The ability of the proposed modified carbon paste electrode to preconcentration of Ag(I) was investigated. Figure 2 shows the differential pulse stripping voltammetry of unmodified CPE (*a*), MCPE (with nanotube and without ACABP) (*b*), ACABP-CPE (without nanotube and with ACABP) (*c*), ACABP-MCPE (with nanotube and ACABP) (*d*) and ACABP-MCPE (with nanotube and ACABP, no Ag(I) in accumulation medium) (*e*) in 0.2 mol L^{-1} HCl after preconcentration in accumulation medium (50.0 ng mL^{-1} Ag(I)).

In CPE case, a small anodic peak at about $+0.06$ V indicates that some adsorption of Ag(I) occurred at the CPE surface. However, this small peak provided an evidence for the absence of a significant preconcentration of Ag(I) at the surface of unmodified electrode. In contrast, when ACABP-CPE (without nanotube) was applied, a well-defined anodic stripping peak at $+0.06$ V appeared after accumulation in the medium containing 50.0 ng mL^{-1} Ag(I). This peak was observed due to the reoxidation of elemental silver, produced by reduction of the accumulated Ag(I) at the negative potentials. As can be seen, the anodic peak current of silver at ACABP-CPE surface is several times larger than the unmodified electrode and when ACABP-MCPE (with nanotube and ACABP) was applied, peak current showed a well increase after accumulation in the medium containing 50.0 ng mL^{-1} Ag(I). The only residual current was observed (Fig. 2e) when ACABP-MCPE was applied in the absence of Ag(I) ions.

3.2. Principle of the Method

The performance of the newly developed ACABP-MCPE is based on the preconcentration of Ag(I) from aqueous solution at the surface of the modified electrode by complex formation with the modifier. The modifier acts as the ligand and the metal ions are the central atoms. The principle of the method involves three steps:

(1) Accumulation step via complex formation:



(2) Reduction step in negative potentials:

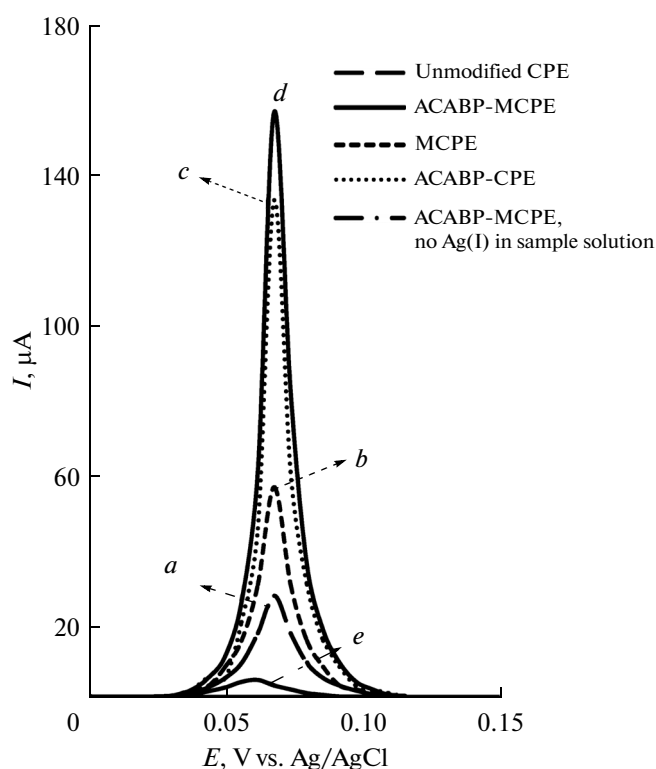
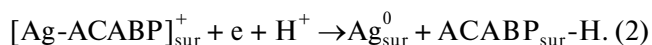
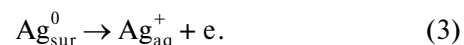


Fig. 2. DP anodic stripping voltammograms in 0.2 mol L^{-1} HCl: (*a*) unmodified CPE with 50.0 ng mL^{-1} Ag(I), (*b*) modified CPE with multi-walled carbon nanotubes (MCPE) with 50.0 ng mL^{-1} Ag(I), (*c*) modified CPE with ACABP (ACABP-CPE) with 50.0 ng mL^{-1} Ag(I), (*d*) modified CPE with multi-walled carbon nanotubes and ACABP (ACABP-MCPE) with 50.0 ng mL^{-1} Ag(I), (*e*) ACABP-MCPE, no Ag(I) in sample solution. Other experimental conditions are: -0.9 V reduction potential, 5 min accumulation time, 30 mV s^{-1} scan rate, 100 mV pulse amplitude and 4 ms pulse period.

(3) Stripping step via positive scan:



In these equations, “aq” and “surf” subscripts mean that the compound is in solution or at the electrode surface.

3.3. Optimization of Analytical Conditions

3.3.1. Effect of electrode composition. The effect of the chemically modified electrode composition in voltammetric behavior was investigated by differential pulse anodic stripping voltammetry of 50.0 ng mL^{-1} Ag(I) in 0.2 mol L^{-1} HCl. As can be seen from Fig. 3, the anodic peak current increased with increasing the amount of chelating agent because the concentration of ACABP at the surface of the modified electrode increases correspondingly. At the range 5 – 10% of ACABP, relative to the mass of the electrode, the largest peak current was obtained. However, the continuous increasing of modifier amount causes a decrease of

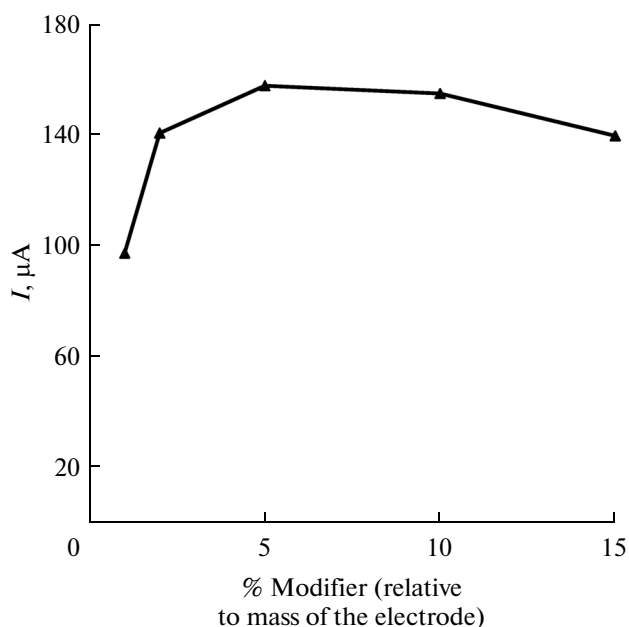


Fig. 3. The effect of modifier amount on the ACABP-MCPE peak current. Other conditions were the same as in Fig. 2.

peak current. Therefore, 5% (w/w) was chosen as the optimum amount of chelating agent in carbon paste composition.

Moreover, the effect of the CNT and graphite amount in carbon paste composition was evaluated. The results showed that the best anodic peak with highest sensitivity obtained with 5% (w/w) for CNT and 50–70% (w/w) for graphite powder. According to these results, a carbon-paste composition of 60 wt % graphite powder, 5 wt % MWCNT, 5 wt % chelating agent and 30 wt % silicon oil was used in further experiments.

3.3.2. Stripping medium. The effects of different electrolytes, such as HCl, HNO₃, CH₃COOH and H₃PO₄ on the stripping peak currents of silver were investigated. The results show that Ag(I) has the best electrochemical responses in HCl. When the measurements were performed in this electrolyte, the largest stripping peak current, the lowest background current and the best shape of peak were obtained.

Also, the effect of supporting electrolyte concentration on the voltammetric response of the ACABP-MCPE was studied over a concentration range between 0.01 and 5.0 mol L⁻¹ in a solution containing 50.0 ng mL⁻¹ Ag(I). The results show that the maximum anodic peak currents were observed at 0.2 mol L⁻¹ of HCl (Fig. 4). Therefore, only a 0.2 mol L⁻¹ of HCl was used in the further studies.

3.3.3. Effect of reduction potential. The influence of reduction potential on the anodic peak current of silver(I) was studied by varying the reduction potential from -0.3 to -1.2 V. When the potential was increased

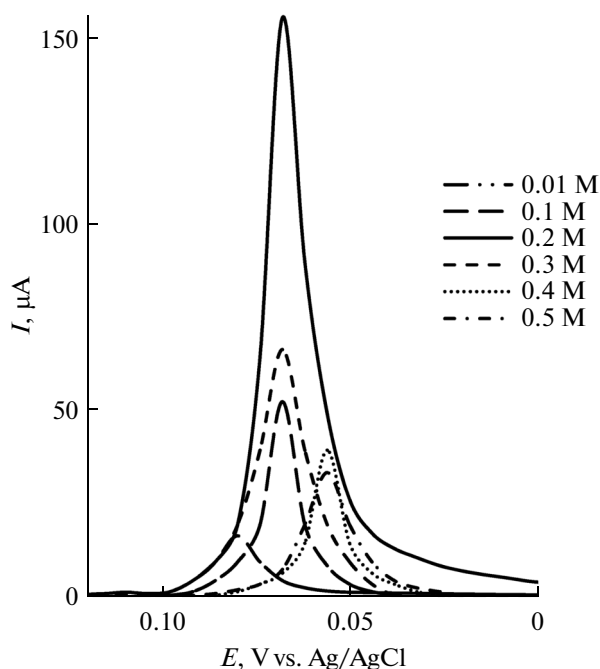


Fig. 4. The effect of stripping medium concentration on the ACABP-MCPE peak current. Other conditions were the same as in Fig. 2.

to -0.9 V, a well-defined peak with the highest peak current was obtained. A further increase in the potential from -0.9 to -1.2 V, was led to decreased peak currents. Therefore, -0.9 V was employed as an optimum potential for further studies.

3.3.4. Effect of accumulation time. The dependence of anodic peak current with the accumulation time for 50.0 ng mL⁻¹ Ag(I) was also investigated. Based on the resulting data, the anodic peak current of Ag(I) was found to increase linearly with the time up to 5 min and remaining constant for longer times. Thus, the accumulation time of 5 min was chosen for all subsequent analysis.

3.3.5. Interference study and reproducibility. The selectivity and utility of the proposed method were investigated in the presence of various cations and anions. For this purpose, the effect of diverse ions, at an initial mole ratio of 500-fold (ion/silver), on the recovery of 50.0 ng mL⁻¹ of Ag(I) from 25.0 mL of aqueous solution was studied. The results of these experiments are summarized in Table 1. As the results indicate, the recovery of Ag(I) was quantitative in the presence of excessive amount of possible interferences from cations and anions. However, 250 times of Cu²⁺ and 350 times of Hg²⁺ and Fe³⁺ were found to reduce the Ag(I) response those are not too high. This indicates that the ACABP-MCPE is a selective sensor for Ag(I) determination. Thus, the method is suitable for the separation and determination of Ag(I) from various matrices.

Table 1. Effect of coexisting ions

| Ion | Recovery, % |
|------------------------------|-------------|
| Fe ³⁺ | 97.2 |
| Cd ²⁺ | 99.3 |
| Na ⁺ | 98.9 |
| Zn ²⁺ | 100.0 |
| Cr ³⁺ | 101.2 |
| Ni ²⁺ | 99.4 |
| Hg ²⁺ | 96.2 |
| Pb ²⁺ | 101.5 |
| Al ³⁺ | 96.0 |
| Mg ²⁺ | 99.8 |
| Mn ²⁺ | 97.2 |
| Cu ²⁺ | 103.5 |
| NO ₃ ⁻ | 101.3 |
| F ⁻ | 95.3 |
| NO ₂ ⁻ | 99.6 |

Mole ratio of ion/silver: 500-fold.

Experimental conditions: 50.0 ng mL⁻¹ of Ag(I), 25.0 mL sample volume, -0.9 V reduction potential, 5 min accumulation time, 30 mV s⁻¹ scan rate, 100 mV pulse amplitude and 4 ms pulse period.

3.3.6. Performance characteristics. Standard solutions containing Ag(I) were prepared in 0.2 mol L⁻¹ HCl. The differential pulse stripping voltammetric determination of a series of standard solutions of Ag(I) was performed after the optimization of the experimental parameters. As can be seen from Fig. 5, the calibration plot was found to be linear between 0.5 and 270 ng mL⁻¹. The detection limit was calculated by making replicate current measurements at -0.9 V for blank solution and based on three times the mean of these measurements gave a value of 0.079 ng mL⁻¹ Ag(I). The equation of calibration graph was $I(\mu\text{A}) = 2.7748c(\text{ng mL}^{-1}) + 4.4259$ with $R^2 = 0.9981$. The precision expressed as the relative standard deviation (RSD) was $\pm 2.4\%$ for seven successive measurements of the same samples containing 50.0 ng mL⁻¹ Ag(I). This result indicates a good reproducibility in the modified electrode construction possibly due to the strong adsorption of Ag(I) ions at the electrode surface.

3.3.7. Analytical applications. In order to establish the validity of the procedure, the proposed method was applied to preconcentration and determination of silver in water samples (tap water, well water and wastewater) and tea leaves with diverse matrix cation and anion concentrations. The reliability of the method was checked by the analysis of the samples spiked with the known amount of silver. The results illustrated in Table 2 reveal that recoveries of spiked samples at 95% confidence level are satisfactory.

To verify the accuracy of the method, this procedure was also applied to the determination of silver in a certified reference alloy; MA-1b reference gold ore

Table 2. Determination of silver in water samples and tea leaves

| Sample | Spiked | Found ^a | Recovery, % |
|-------------------------|--------|--------------------|-------------|
| ng mL ⁻¹ | | | |
| Tap water ^c | 0.0 | N.D. ^b | — |
| | 25.0 | 25.3 \pm 0.8 | 101.2 |
| | 50.0 | 48.1 \pm 1.1 | 96.2 |
| Well water ^d | 0.0 | N.D. ^b | — |
| | 25.0 | 24.8 \pm 0.7 | 99.2 |
| | 50.0 | 48.9 \pm 1.1 | 97.8 |
| Wastewater ^e | 0.0 | 11.4 \pm 0.4 | — |
| | 25.0 | 35.9 \pm 1.0 | 98.0 |
| | 50.0 | 63.2 \pm 1.5 | 103.6 |
| ng g ⁻¹ | | | |
| Tea leaves | 0.0 | 134.2 \pm 3.9 | — |
| | 25.0 | 158.3 \pm 4.4 | 96.4 |
| | 50.0 | 182.9 \pm 4.7 | 97.4 |

^a Mean \pm standard deviation ($n = 3$).

^b N.D.: Not Detected.

^c Kerman drinking water, Kerman, Iran.

^d Shahid Bahonar University of Kerman, Kerman, Iran.

^e Iron factory, Bafgh, Yazd, Iran.

Experimental conditions were the same as in Table 1 except the Ag(I) concentration and sample volume.

and the analytical results are given in Table 3. As can be seen, the obtained results are in good agreement with the reference values and there is no significant

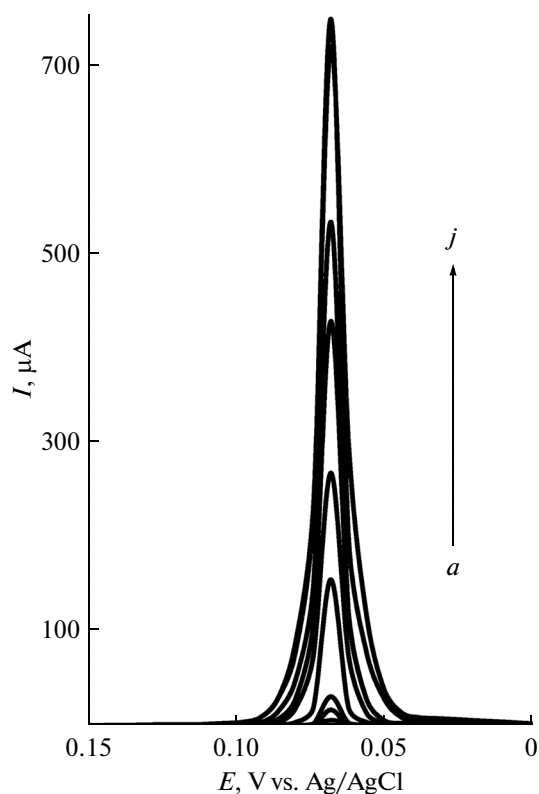


Fig. 5. DP anodic stripping voltammograms of ACABP-MCPE, concentrations of (a–j): 0.5, 1.0, 5.0, 10.0, 50.0, 100.0, 150.0, 200.0, 250.0, and 270.0 ng mL⁻¹ of Ag(I).

Table 3. Analysis of silver in a certified reference material

| Sample | Composition | Found ^a | Recovery, % |
|--------------------------|--|--------------------|-------------|
| MA-1b reference gold ore | Si; 24.5, Al; 6.11, Fe; 4.62, Ca; 4.60, K; 4.45, Mg; 2.56, C; 2.44, Na; 1.49, S; 1.17, Ti; 0.38, Ba; 0.18, P; 0.16, Mn; 0.09% Cr; 200.0, Pb; 200.0, Rb; 160.0, Zr; 140.0, Cu; 100.0, Zn; 100.0, Bi; 100.0, Ni; 90.0, Mo; 80.0, Te; 40.0, Co; 30.0, Y; 20.0, W; 15.0, Sc; 13.0, As; 8.0, Au; 17.0, Sb; 3.0. Ag; 3.9 $\mu\text{g g}^{-1}$ | 3.8 \pm 0.1 | 97.4 |

^a Mean \pm standard deviation, $n = 3$.

Experimental conditions were the same as in Table 1 except the Ag(I) concentration and sample volume.

Table 4. Comparison of the proposed method with other reported analytical methods for silver determination

| Analysis method | RSD, % | Linear range, ng mL^{-1} | LOD, ng mL^{-1} | Ref. |
|----------------------|---------|-----------------------------------|--------------------------|-----------|
| Pot ^a | 2.7–3.8 | 11.9–107900 | 7.5 | [2] |
| FAAS | 2.14 | 3–200 | 0.56 | [5] |
| ETAAS | 2–10 | >20 | 0.08 | [6] |
| Spect. ^b | 10.2 | 50–5000 | 50 | [15] |
| Spect. | 1.67 | 10–600 | – | [16] |
| FAAS | 3.8 | 5–20 | 0.22 | [17] |
| FAAS | 2.0 | 4–220 | 0.7 | [18] |
| FAAS | <3 | 250–5000 | 4.6 | [19] |
| FAAS | 3.1 | 0.5–30.0 | 0.2 | [20] |
| FAAS | 2.1 | – | 1.4 | [21] |
| FAAS | 1.2 | 40–1000 | 1.1 | [22] |
| FAAS | 4.7 | 30–160 | 5 | [23] |
| TSFFAAS ^c | 3.43 | 0.5–40 | 0.15 | [24] |
| SV ^d | 4.8–6.5 | 5.4–215.7 | 5.2 | [25] |
| SV | 1.5 | 70–1000 | 60 | [26] |
| SV | 4.2 | 64.7–258.9 | – | [27] |
| SV | 1.99 | 1.07–1078.6 | 0.19 | [28] |
| SV | 4.1 | 5.4–323.6 | 1.1 | [29] |
| SV | 3.6 | 5.4–107.9 | 2.7 | [30] |
| SV | 2.4 | 0.5–270 | 0.079 | This work |

^a Potentiometry.

^b Spectrophotometry.

^c Thermospray flame furnace atomic absorption spectrometry.

^d Stripping voltammetry.

difference between the results and the accepted values. Thus, the procedure is reliable for analysis of a wide range of samples.

3.3.8. Comparison of ACABP-MCPE with some previously reported. A number of analytical characteristics of the ACABP-MCPE were compared with those of the previously reported Ag(I) determination with other methods [2, 5, 6, 15–30]. The results are summarized in Table 4. As can be seen, the ACABP-

MCPE electrode shows better analytical characteristics such as the lowest detection limit and widest linear range except the following reported [2, 28].

CONCLUSIONS

The anodic stripping voltammetric procedure for the silver determination was proposed. This work demonstrated that the carbon paste electrode modi-

fied with ACABP and MWCNT (ACABP-MCPE) is a suitable alternative for the analytical determination of Ag(I). The proposed sensor has good characteristics such as; wide concentration range (0.5–270 ng mL⁻¹), very low detection limit (0.079 ng mL⁻¹) and good selectivity. This modified electrode (ACABP-MCPE) coupled with differential pulse anodic stripping voltammetry was successfully applied in water, tea leaves and a certified reference material with satisfactory results. In addition, the inherent advantages of the proposed electrochemical sensor are its rapid response, simple operation, precise results, low cost and direct application to the determination of silver.

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