

یک روش جدید برای تعیین ولتامتری عریانسازی یون نقره در الکتروود خمیر نانولوله‌های کربنی اصلاح شده با ۴ و ۶-دی آمینو پیریدین-۲-تیول

علیرضا محدثی

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A New Method for Stripping Voltammetric Determination of Ag(I) at Carbon Nanotube Paste Electrode Modified with 4,6-Diaminopyrimidine-2-Thiol

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چکیده

یک روش ولتامتری عریانسازی آندی پالس تقاضی برای تعیین یون نقره در سطح یک الکتروود خمیر کربن اصلاح شده با ۴ و ۶-دی آمینو پیریدین-۲-تیول و نانولوله‌های کربنی توسعه پیدا کرد. دستورالعمل آنالیز عبارتست از یک مرحله پیش تغلیظ مدار باز از محلول در حال هم خوردن برای مدت ۹ دقیقه. در ادامه الکتروود در محلول جدید قرار گرفته و یون‌های پیش تغلیظ شده نقره با اعمال پتانسیل -0.6 ولت برای ۱۵ ثانیه کاهش می‌شوند. در نهایت یک پیک آندی در اثر روبش پتانسیل از -0.2 به $+0.3$ بدست می‌آید. حد تشخیص روش 0.08 میکروگرم بر لیتر بدست آمد و انحراف استاندارد نسبی برای غلظت‌های 10 و 100 میکروگرم بر میلی لیتر از نقره به ترتیب 2.4 و 1.2 درصد محاسبه شد. منحنی درجه بندی برای غلظت‌های 0.99 تا 118.57 میکروگرم بر لیتر نقره خطی بود و روش حاضر برای تعیین یون‌های نقره در آلیاژهای استاندارد و نمونه‌های آبی بکار رفت.

واژه‌های کلیدی

نانولوله‌های کربنی؛ ولتامتری عریانسازی آندی؛ الکتروود خمیر کربن اصلاح شده؛ یون نقره.

Abstract

A differential pulse anodic stripping voltammetric method was developed for the determination of Ag(I) at a carbon paste electrode modified with 4,6-diaminopyrimidine-2-thiol and multi-walled carbon nanotubes. The analysis procedure consisted of an open circuit accumulation step in stirred sample solution for 9 min. This was followed by medium exchange to a clean solution where the accumulated Ag(I) was reduced for 15 s in -0.6 V. Subsequently an anodic potential scan was affected from -0.2 to $+0.3$ V to obtain the voltammetric peak. The detection limit of silver(I) was $0.08 \mu\text{gL}^{-1}$ and R.S.D. for 10 and $100 \mu\text{gL}^{-1}$ Ag(I) were 2.4 and 1.2%, respectively. The calibration curve was linear for 0.99 – $118.57 \mu\text{gL}^{-1}$ Ag(I). The procedure was applied to determination of Ag(I) in standard alloys and water samples.

Keywords

Carbon Nanotube; Anodic Stripping Voltammetry; Modified Carbon Paste Electrode; Ag(I).

1. INTRODUCTION

Trace metal pollution in environmental sources like water, air and soil has affected the life on earth [1-2]. The contamination of the environment with toxic heavy metals is a major environmental problem [3-4]. Silver is one of the industrially important elements. The widespread use of silver compounds and silver-containing procedures in industry, medicine, jewelry, cloud seeding and in the disinfection of drinking water has resulted in an increasing silver content of environmental samples. It is used for the preparation of

corrosion-resistance alloys and its compounds are extensively used in the processing of foods, drugs, beverages and in filters and other equipments to purify water. Consequently, determination of trace amounts of silver is important for many areas of chemical analysis and simple and highly sensitive methods are needed to monitor the Ag levels in samples at ever decreasing concentrations. Trace and ultra-trace amount of silver ions in environmental samples is a stimulant for applying preconcentration techniques prior to its determination [5]. The most

widely used techniques for separation and preconcentration of trace amount of silver ions are coprecipitation [6], solid-phase extraction (SPE) [7], liquid-liquid extraction (LLE) [8] and cloud point extraction (CPE) [9]. However, most of these procedures are time-consuming and may cause sample contamination. Several atomic spectrometric techniques such as atomic absorption spectrometry [10], inductively coupled plasma atomic emission spectrometry (ICP-AES) [11] and inductively coupled plasma mass spectrometry (ICP-MS) [12] have been used for the determination of silver in different environmental samples. Two limitations in these techniques are lower levels of analyte ions than the quantitation limits of the technique and the interferic effects of the main components of the samples [13].

Stripping voltammetric analysis is one of the most sensitive methods for determining ion metals [14]. The modified carbon paste electrodes (MCPEs) analysis has attracted considerable attention in recent years [15]. MCPEs have several advantages such as non-toxic, low background current, wide range of used potential, rapid renewal and easy fabrication [16-17]. Main reasons for modification are to improve the selectivity and sensitivity of the electrochemical measurements by preconcentrating the target analyte from a dilute solution on the electrode surface. The accumulation step preceding the measurement can be performed with or without an applied potential (closed or open circuit condition) depending on the nature of the preconcentration. In open circuit condition it is possible to separate the analyte from interference species under the special condition and following a medium exchange for stripping of accumulated analyte [14,17]. Nowadays, carbon nanotubes (CNTs) have also been used in carbon paste electrodes [18-20]. CNTs have very interesting properties, such as ordered structure with high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity and high surface area [21-23]. Applying the CNT in carbon paste electrode, increases the surface area, conductivity, current and finally improves the method sensitivity. A number of articles discuss about the determination of silver by stripping analysis at modified carbon paste electrodes. There are carbon paste electrodes modified by p-isopropylcalix [24] arene [25], NABHE [24] 4-(2-pyridylazo)-resorcinol [26], polythiophene [27], dl-dithiothreitol [28], 3-amino-2-mercaptoquinazolin-4(3H)-one [29] and N,N'-diphenyl oxamide [30].

We describe here a simple and effective carbon paste electrode modified with CNT and 4,6-diaminopyrimidine-2-thiol (DAPT) (Fig. 1), DAPT-MCPE, was developed and the sensor was applied to the determination of Ag(I) by using differential pulse anodic stripping voltammetry (DPASV). The modifier, DAPT, can preconcentrate Ag(I) from aqueous solution to the surface of the modified electrode and greatly increase the sensitivity of determination. In addition, the DAPT-MCPE exhibited several advantages such as simple preparation, reproducibility of surface renewal by simple polishing, good stability and excellent ability to determine ultra-trace amounts of silver in standard alloys and water samples.

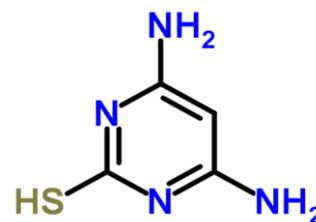


Fig. 1. 4,6-diaminopyrimidine-2-thiol (DAPT) structure.

2. EXPERIMENTAL

2.1. Instrumentation and apparatus

All voltammetric experiments were performed using a Metrohm Computrace Voltametric Analyzer Model 757 VA. The electrochemical cell consisted of a DAPT-MCPE as a working electrode, Ag/AgCl/KCl (saturated) as a reference electrode and a platinum wire as an auxiliary electrode. A Metrohm Computrace Voltametric Analyzer Model 757 VA was used. A Metrohm 713 pH meter was used for pH adjustments. A stirrer (Jenway, Germany) was used to stir solutions in the accumulation step.

2.2. Materials and reagents

The stock solution of 1000 mg L^{-1} Ag(I) was prepared from AgNO_3 in deionized water. The accumulation solution for silver(I) was acetate buffer (0.1 M, pH 4.1). High purity nitrogen was used for deaeration. The chelating agent, DAPT, was purchased from Merck and MWCNTs (95% purity) with an average outer diameter of 3–20 nm, length of 1–10 μm , number of walls 3–15, and surface area of $350 \text{ m}^2 \text{ g}^{-1}$ were prepared from Palasmachem GmbH (Berlin, Germany). Nafion perfluorinated ion exchange resin (5.0 wt% solution in lower aliphatic alcohols/ H_2O mixture) was purchased from Merck. All reagents used were of analytical grade and were used directly without further purification.

2.3. Preparation of CPE and DAPT-MCPE

Modified carbon paste was prepared by mixing 30 μL of silicon oil with 1 g of high purity graphite powder, 0.07 g chelating agent and 0.5 g MWCNT (for increasing the current and sensitivity) and following hand mixing in a mortar and pestle. A liquid for use as pasting agent in a carbon paste electrode should fulfill certain conditions. They should be sufficiently chemically inert, insulating, non-volatile, water immiscible and forming paste mixtures of fine consistency. However, there also are some less favorable characteristics of pastes made from paraffin oils or Nujol; for instance, their vulnerability in media with organic solvents. In this respect, better experience has been gained with silicon oil-based carbon pastes that also represent quite common type of pasting liquid [31]. 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. The blank electrode (CPE) was prepared using the same procedure with the exception of using DAPT.

2.4. General procedure

For DPASV experiments, the DAPT-MCPE was immersed in a 20 ml of sample solution (0.1 M acetate buffer, pH 4.1) containing a known amount of Ag(I) and the solution was stirred for 9 min. This was followed by medium exchange to a 0.1 M stripping solution (0.1 M KNO_3 , 0.1 M acetate buffer, pH 4.1) where the accumulated silver(I) was reduced for 15 s in -0.6V . Finally the differential pulse voltammogram was recorded from -0.2 to $+0.3$ V (with 20 mVs^{-1} scan rate, 100 mV pulse amplitude, and 5 ms pulse period). All measurements were carried out at room temperature ($\sim 25^\circ\text{C}$).

3. RESULT AND DISCUSSION

3.1. Voltammetric behavior of silver(I) at the DAPT-MCPE

The ability of the DAPT-MCPE to preconcentrate Ag(I) was investigated. Fig. 2(a) and (b) show the DPA voltammograms of DAPT-MCPE and CPE in stripping solution (0.1 M KNO_3 , 0.1 M acetate buffer, pH 4.1) after preconcentration in the blank accumulation medium. In the potential range studied, only residual current was observed. Fig. 2(c) and (d) show the DPA voltammograms obtained with the same procedure at the MCPE and DAPT-MCPE but with $100 \mu\text{gL}^{-1}$ Ag(I) in the accumulation medium. In CPE case, a small

anodic peak could be discerned at about $+0.13\text{V}$ indicating some adsorption of Ag(I) could have occurred at the CPE surface. However, this miniscule peak provided evidence for the absence of significant preconcentration of Ag(I) at the unmodified electrode. In contrast when DAPT-MCPE was applied, a well-defined anodic stripping peak with peak potential of $+0.14\text{V}$ appeared after accumulation in the medium containing $100 \mu\text{gL}^{-1}$ Ag(I). This peak was due to the reoxidation of elemental silver produced by the reduction of accumulated Ag(I) at the negative potentials. As can be seen, the anodic peak current of silver at DAPT-MCPE is nearly six times larger than that of CPE. Thus, there is a substantial enhancement in silver oxidation peak current when carbon paste electrode was modified with CNT and DAPT. Hence, the anodic peak of Ag(I) was systematically studied by differential pulse anodic stripping voltammetry for analytical applications.

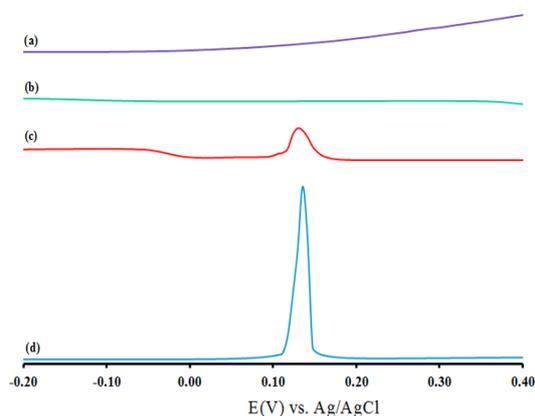


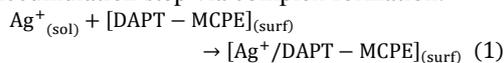
Fig. 2. DPA voltammograms in stripping solution (0.1 M KNO_3 , 0.1 M acetate buffer, pH 4.1) after open circuit accumulation in acetate buffer (pH 4.1): (a) DAPT-MCPE, no Ag(I) in accumulation medium, (b) CPE, no Ag(I) in accumulation medium, (c) CPE, with $100 \mu\text{gL}^{-1}$ Ag(I) in accumulation medium, and (d) DAPT-MCPE with $100 \mu\text{gL}^{-1}$ Ag(I) in accumulation medium. Other conditions: accumulation time = 9 min; reduction time = 15 s and scan rate = 20 mVs^{-1} .

3.2. Principle of method

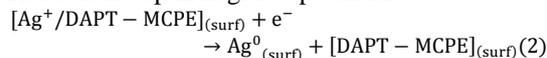
The performance of the newly developed DAPT-MCPE is based on the preconcentration of Ag(I) from aqueous solution onto the surface of the modified electrode by forming complexes with the modifier. The modifier acts as the ligand and the metal ions are the central atom. In the other hand, the surface concentrations of Ag(I) are much larger than those of the unmodified electrode and the sensitivity is greatly increased. Regarding the above-discussed observations and under the experimental conditions, the possible pathways for analysis cycle, from accumulation

step to voltammetric scan, can be presented as follows:

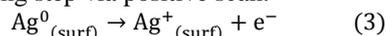
Accumulation step via complex formation:



Reduction step in negative potentials:



Stripping step via positive scan:



3.3. Optimization of analytical conditions

To optimize the performance of the DAPT-MCPE, for the electrochemical determination of Ag(I) in aqueous solution, the parameters influencing the response of the electrode including amount of modifier, accumulation medium, pH of solution, , accumulation time, reduction potential and time were investigated.

The accumulation of Ag(I) at the DAPT-MCPE was based on the complex formation between the metal ion and the modifier. Therefore, the amount of modifier in the carbon paste had significant influence on the voltammetric response of the modified electrode. The results showed that the peak current increased as the amount of modifier increased from 0 to 7 mg due to the increase accumulation sites and then reached an approximate plateau from 7 to 12 mg. However, the peak current decreased when the amount of modifier exceeded 12 mg, because the excessive modifier may be reduced the conductivity of the modified electrode. So, the best amount of the modifier in carbon paste composition is 7 mg.

The effect of some Accumulation media, such as oxalate, sulfate, ammonia, phosphate and acetate buffers on stripping peak currents of silver were investigated. The results show that Ag(I) have the highest current in 0.1M of acetate buffer.

The influence of pH on the stripping peak current was studied in buffer solutions (pH range 2.1-8.2). Current-pH plot (Fig. 3) reveals that, within the pH range 3.5-4.7, the current did not vary significantly. Therefore the electrode response is independent of pH in this range and all subsequent measurements were made in pH 4.1.

When the DAPT-MCPE is immersed in a solution containing Ag(I), interaction occurs between the Ag ions and DAPT. The longer the electrode is exposed to the solution containing the analyte, the more Ag(I) is accumulated on the surface, which consequently yields a higher current. We studied the dependence of the anodic stripping peak current on the preconcentration time for two different Ag(I) concentrations. The peak current was found to increase with increasing preconcentration time, indicating an enhancement of Ag(I) uptake at the electrode surface.

Normally, the increase in the response current continues until a maximum signal level (presumably corresponding to either saturation or an equilibrium surface coverage) is attained. As shown in Fig. 4, the attainment of a steady state accumulation level of Ag(I) at the electrode surface requires an exposure time of 9 min for $100 \mu\text{gL}^{-1}$ and $10 \mu\text{gL}^{-1}$ Ag(I). Hence, preconcentration time of 9 min was employed in all subsequent experiments.

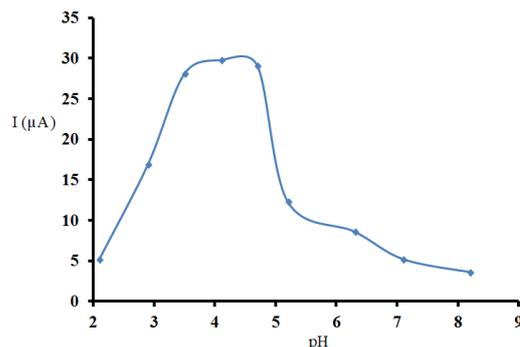


Fig. 3. The pH effect of accumulation medium on the DPAV currents. Other conditions as in Fig. 2.

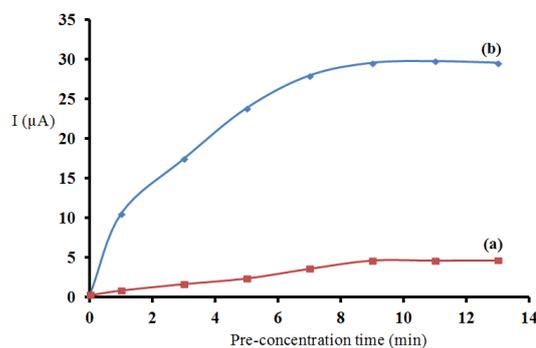


Fig. 4. Plot of DPA peak currents vs. accumulation time. Ag(I) concentrations were (a) 10 and (b) $100 \mu\text{gL}^{-1}$. Other conditions as in Fig. 2.

The influence of reduction potential on the anodic peak current of silver(I) was studied by varying the reduction potential from 0.1 to -0.9 V . When the potential was increased to -0.6 V , a well-defined peak with the highest peak current was obtained. Further increase in the reduction potential led to decreased peak currents. This is mainly due to the cohydrogen evolution at such high potentials. Therefore, -0.6 V was employed as an optimum reduction potential for further studies.

The effect of the reduction time was studied for Ag concentration of $100 \mu\text{gL}^{-1}$ at standard measuring conditions. The time of reduction was changed from 0 to 21 s. It was found that the silver peak current increases linearly with the reduction time up to 15 s. For further study a reduction time of 15 s was chosen.

3.4. Performance characteristics

In order to obtain an analytical curve for our developed method, The differential pulse stripping voltammetric determination of a series of standard solutions of Ag(I) was performed after the optimization of the experimental parameters. The best results were obtained under the following optimized conditions: 15 s reduction time, -0.6 V reduction potential, 9 min accumulation time and 20 mVs⁻¹ scan rate in 0.1 M acetate buffer with pH 4.1 containing 0.1 M KNO₃. Standard solutions containing different amounts of Ag(I) were prepared in pH 4.1 and the general procedure was applied to these solutions. Voltammograms at these concentrations are shown in Fig. 5.

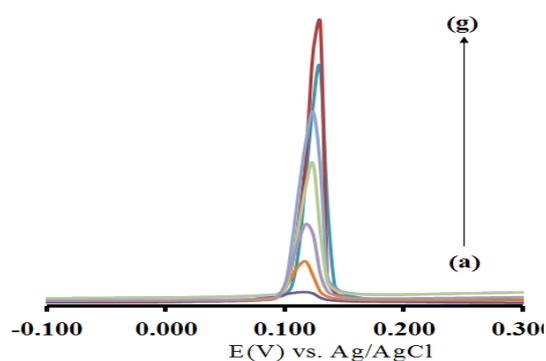


Fig. 5 DPA stripping voltammograms of DAPT-MCPE, concentrations of a–g: 0.99, 11.98, 27.92, 55.68, 79.36, 99.01 and 118.57 μgL^{-1} of Ag(I). Other conditions as in Fig. 2.

Under optimized conditions, the suggested method showed a typical linear response ranging from 0.99 to 118.57 μgL^{-1} . The equation of calibration graph was $y = 0.2759x + 1.8348$, where y and x are the peak current (μA) and x Ag(I) concentration (μgL^{-1}), respectively. The linear correlation coefficient was 0.9994. A detection limit of 0.08 μgL^{-1} was determined using a $3s_b/\text{slope}$ ratio where s_b is the standard deviation of the mean value for current of the blank. The precision expressed as the relative standard deviation (R.S.D) for 10 and 100 μgL^{-1} Ag(I) were 2.4 and 1.2%, respectively. This result indicates a good repeatability in the modified electrode construction possibly due to the strong adsorption of the Ag(I) in the electrode surface.

3.5. Interference study

The presence of other metal ions could interfere with Ag(I) determination if they compete for complexation at the DAPT complexing sites. The criterion for interference of each ion was set at $\pm 5.0\%$ in the obtained recovery for a solution containing Ag (I), without any interfering. The results showed that When the developed procedure was employed for the determination of

150 μgL^{-1} Ag(I) with optimum conditions, no interference was encountered for additions of 500 μgL^{-1} each of Ni(II), Pb(II), Zn(II), Mn(II), Co(II), Au(III), Na(I), Bi(III), Fe(II), K(I). However, the presence of 500 μgL^{-1} Cu(II) and Hg(II) caused 21 and 19% depressions of the Ag(I) peak, respectively.

3.6. Validity of method

Various standard reference materials were analyzed for checking the reliability of method. Standard reference materials including SRM 127b Solder (40Sn-60Pb), SRM 464 Low-alloy steel and SRM 54d Tin-base alloy were analyzed for Ag(I). The 0.20 g standard alloy was dissolved completely in 10 mL hydrochloric acid:water (1:1) by heating it on a water bath and then 1 mL of 30% (v/v) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on a water bath. The solution was cooled, filtered, and diluted to 100 mL distilled water in a standard flask. An aliquot of this sample was added to 20 mL of 0.1 M acetate buffer with pH 4.1, and general procedure was used on resultant solution. The obtained results are given in Table 1. These results are in agreement with certified values and confirm that the proposed method has good accuracy.

Table 1. Determination of Ag(I) in standard alloys.

Sample	Found Ag(I) (%)	Recovery (%)
SRM 127b Solder (40Sn-60Pb)	0.0098 \pm 0.0002	98.3
SRM 464 Low-alloy steel	0.0031 \pm 0.0005	98.6
SRM 54d Tin-base alloy	0.0032 \pm 0.0005	100.4

3.7. Analytical application

In order to evaluate the performance of DAPT-MCPE in practical analytical applications, quantitation of Ag(I) in several water samples was determined. Reliability was checked by spiking the sample and the accuracy of the method was examined by recovery experiment. The results are given in Table 2. As can be seen, the ability of the method for the analysis of Ag(I) in real matrix is satisfactory.

Table 2. Determination of Ag(I) in real water samples.

Sample	Spiked ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$) ^a	Recovery (%)
Drinking water ^b	0.0	N.D.	-
	100.0	101.3 \pm 1.9	101.3
Laboratory water ^c	0.0	N.D.	-
	100.0	104.5 \pm 1.8	104.5

ND not detected

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

^b Kerman drinking water, Kerman, Iran

^c Payame Noor University of Kerman, Kerman, Iran

4. CONCLUSIONS

The anodic stripping voltammetric procedure for the silver determination was investigated. We describe here that carbon paste electrode modified with DAPT and MWCNT is a suitable alternative for the analytical determination of Ag(I). This developed sensor have good characteristics such as wide concentration range (0.99–118.57 μgL^{-1}), very good detection limit (0.08 μgL^{-1}) and good selectivity coefficient for many cations, because of the complexation and the exchange of the medium. This modified electrode, DAPT-MCPE, coupled with differential pulse anodic stripping voltammetry was successfully applied in drinking and laboratory water samples and standard reference materials and the results were satisfactory. In addition, the inherent advantages of the developed electrochemical sensor are its rapid response, simple operation, precise results, low cost and direct application to the determination of Ag(I).

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