Innovare Academic Sciences

International Journal of Pharmacy and Pharmaceutical Sciences

ISSN- 0975-1491 Vol 6, Issue 3, 2014

Original Article

DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRIC DETERMINATION OF SELENIUM(IV) AT A GOLD ELECTRODE MODIFIED WITH 3, 3′-DIAMINOBENZIDINE.4HCL-NAFION

ABDUL AZIZ RAMADAN[1]*, HASNA MANDIL[2], ABDULRAHMAN SHIKH-DEBES

Dept. of Chemistry, Faculty of Sciences, Aleppo University, Syria. Email: dramadan@scs-net.org, mandil@scs-net.org

Received: 02 Feb 2014, Revised and Accepted: 27 Apr 2014

ABSTRACT

Differential pulse anodic stripping voltammetric Analysis (DPASVA) of selenium(IV) using a gold electrode modified with 3,3′-diaminobenzidine.4HCl-nafion (GEMDN) has been studied. Various parameters (electrolyte, deposition time, pulse duration, pulse amplitude, etc.) affecting the Se(IV) determination were examined. Selenium(IV) was determined in an aqueous $HClO_4$ (0.2M) medium of pH 0.22 at an accumulation potential of -200 mV and an accumulation time of 200 s. Under the optimum conditions, liner calibration graph, $I_p=f(C_{Se4}+)$, was obtained in the concentration ranges of $5x10^{-9}$ M (0.3948 ng.mL^{-1}) to $2x10^{-6}$ M (157.92 ng.mL^{-1}) with relative standard deviations (RSD) ≤ 4.6%, and the detection limit was 0.06 ng.mL^{-1}. This method showed a good accumulation efficiency for selenium and good resistance to interferences from metal ions as well as those associated with selenium in pharmaceuticals. The results for the determination of Se^{4+} using GEMDN were more sensitive and accurate than that obtained using bare gold electrode; the sensitivity was increased about 20000 times.

Keywords: 3, 3′-Diaminobenzidine.4HCl, Nafion, Selenium, Differential pulse anodic stripping voltammetry.

INTRODUCTION

The performance of a poly(1,8-diaminonaphthalene)-modified gold electrode (pDAN-Au) for the determination of the selenium(IV) ion in an aqueous medium was investigated with anodic stripping voltammetry without the pretreating of the sample. The detection limit employing the anodic stripping differential pulse voltammetry was 9.0 x10^{-9} M for Se(IV) with 4.4 % of RSD [1].

Differential pulse cathodic stripping voltammetric determination of selenium from pharmaceutical products was applied. The drug samples were treated with a mixture of 6 ml HNO_3 and 1 ml H_2O_2 in the microwave oven. The peak potential is -0.545 V vs. Ag/AgCl, and the calibration curve is linear up to 0.125 ng.mL^{-1}, but selenium was determined in the range 8 to 64 ng.mL^{-1} in pharmaceutical products [2].

Electropolymerization of 3,3′-diaminobenzidine on a gold surface gave an adherent, stable film of poly(3,3′-diaminobenzidine) (PDAB). This polymer film retained the complexational functionalities of its monomer, demonstrating preconcentration abilities for several ions, including Se(IV) and Te(IV). In particular, in this work, continuous flow and flow injection methods were developed for the sensitive and selective determination of Te(IV). The optimized method for the continuous flow mode had a detection limit of 5.6×10^{-9} mol.L^{-1} for 10 min preconcentration. Typical relative standard deviations for six consecutive determinations were 1.82 and 2.56% for Te(IV) concentrations of 1.0×10^{-6} and 5.0×10^{-8} mol.L^{-1}, respectively (10 min preconcentration). The method was applied to the determination of Te(IV) in real samples [3]. Determination of Se(IV) was investigated on 3,3'-diaminobenzidine/Nafion/ mercury film modified glass carbon electrode (DNMFE). The 3,3'-diaminobenzidine/ Nafion coating solution was irradiated by a tungsten light bulb to oxidize the 3,3'-diaminobenzidine. This coating solution was then spin-coated onto glass carbon electrode. Mercury was electrodeposited onto the electrode surface. Selenium(IV) was preconcentrated onto the DNMFE from the sample solution staturated with EDTA at an accumulation potential of -0.350 V, and determined by cathodic square-wave stripping voltammetry (SWSV). The analytical signal was linear from 1 to 300 ∝g.L^{-1} with 5 min accumulation [4]. Determination of Se^{4+} by pulse anodic stripping voltammetry with constant amplitude of negative polarity (SVPNP) using a Vitamin E–Nafion modified gold electrode has been studied. Selenium(IV) was determined in a aqueous $HClO_4$ medium (pH=1.1) at an accumulation potential of -240 mV and an accumulation time of 300 sec. The analytical signal was linear from in the concentration ranges of $1x10^{-7}$ to $8x10^{-6}$ mol.L^{-1} with relative standard deviations (RSD) ≤ 5.2% [5].

Differential pulse anodic stripping voltammetric determination of selenium (IV) using a vitamin E-nafion modified gold electrode has been studied. Selenium (IV) was determined in an aqueous $HClO_4$ medium of pH 1.10 at an accumulation potential of -240 mV and an accumulation time of 300 s. Under the optimum conditions, liner calibration graph was obtained in the concentration ranges of 5×10^{-8} -1 × 10^{-5} mol.L^{-1} with relative standard deviations (RSD) 4.5 %. This method shows that the results for the determination of Se^{4+} using vitamin E-nafion modified gold electrode were more sensitive and accurate than that obtained using bare gold electrode. The sensitivity was increased about 200 times [6].

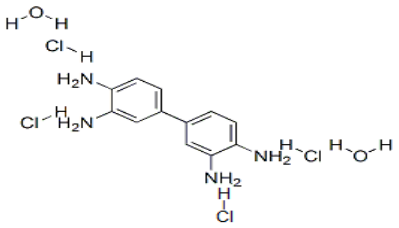
Determination of selenium(IV) in Syrian pharmaceuticals with a methylene blue-nafion modified gold electrode by using different operating modes of pulse anodic stripping voltammetry : with constant amplitude of negative (PASVNP) or positive (PASVPP) polarity, imposed pulses of linearly increasing amplitude (PASVLIA) and differential sampling on successive pulses (ΔI/Δt) was applied. Selenium(IV) was determined in an aqueous $HClO_4$ medium (1 M) at an accumulation potential of -240 mV and an accumulation time of 300s. The potential was scanned from 0.0 to 1250 mV using auto-scan facility. The peak potential was measured at 1000-1010, 1030-1040, 1130-1140 and 1030-1060 mV and the calibration curve for Se(IV) under optimized conditions was linear in the ranges 7.896-78.96, 23.688-118.44, 23.688-118.44 and 0.7896-78.96 ngmL^{-1} for operating modes PASVNP, PASVPP, PASVLIA and ΔI/Δt, respectively. RSD was less than 5 %. The methods were applied to the determination of Se(IV) in Syrian pharmaceuticals with high sensitivity and accuracy. The results obtained by pulse anodic stripping voltammetry methods were validated by atomic absorption spectroscopy with hydride generation [7].

Differential pulse anodic stripping voltammetric (DPASV) determination of selenium(IV) using a methylene blue-Nafion modified gold electrode (MBNMGE) has been studied. Selenium(IV) was determined in an aqueous HClO4 medium (1.0 M) at an accumulation potential of -240 mV and an accumulation time of 300 s. The potential was then scanned from 0.0 to 1250 mV by

differential pulse anodic stripping voltammetry using the auto-scan facility. The peak height was measured at 1030-1060 mV. The calibration graph for Se(IV) under optimized conditions was linear in the range from 1×10^{-8} to 1×10^{-6} mol.L^{-1} (0.79 ng mL^{-1} to 79 ng.mL^{-1}) and was found to obey the equation y = 11.50x + 0.003, where y and x are the peak current (μA) and Se(IV) concentration (μmol.L^{-1} or μM), respectively. The coefficient of determination was $R^2 = 0.999$. The relative standard deviations (RSD) for determination of Se(IV) at the concentration of 1×10^{-8} mol.L^{-1} was 4.2 % (n = 5). The detection limit was 5.0×10^{-9} mol.L^{-1}. This method shows that the results for the determination of Se(IV) using methylene blue-Nafion modified gold electrode were more sensitive and accurate than that obtained using vitamin E-Nafion modified gold electrode (VENMGE) about 5 times and about 1000 times using bare gold electrode [8]. The polarographic and voltammetric analysis was successfully applied for determination some drugs as atorvastatin [9-11], gatifloxacin [12], carbinoxamine maleate [13], dipyrone [14] and lomefloxacin [15]. In the present work, Differential pulse anodic stripping voltammetric Analysis (DPASVA) of selenium(IV) using a gold electrode modified with 3,3′-diaminobenzidine.4HCl-nafion (GEMDN) has been applied.

MATERIALS AND METHODS

Reagents



Scheme 1: 3, 3′-Diaminobenzidine.4HCl.2H$_2$O, (C$_{12}$H$_{14}$N$_4$·4HCl·2H$_2$O), DAB

Nafion perfluorinated ion-exchange resin in ethanol (3%. v/v) was purchased from Aldrich. 3,3′-diaminobenzidine.4HCl.2H$_2$O, mol. mass 396.2 g (Scheme1) was from SERVA Electrophoresis Gmbh (Purety 96.0%). H_2SeO_3 and all other reagents were of analytical grade from Merck. *An HClO$_4$ solution 0.20M* was used at pH=0.22. *A stock solution (a) of Se(IV)* 789.6 μg.mL^{-1} (0.01 mol.L^{-1}) and *A stock solution (b) of Se(IV)* 7.896 μg.mL^{-1} (0.1 mmol.L^{-1}) were prepared using $HClO_4$ solution. A working solution for voltammetric investigations was prepared by dilution of the stock solution of Se(IV) (a or b) with $HClO_4$ solution.

Apparatus

A polarograghic analyzer, model PRG-5 (Tacussel), with increasing amplitude pulses was used for differential detection of current and for superimposing constant amplitude pulses of negative or positive polarity and pulses of linearly increasing amplitude as the source of scanning voltage. A programmer model POLARMAX-78, and a recorder model ECOSRIPT (Tacussel) were also used. A rotating disk gold electrode (RDGE) model DI-65-14 was used as a working electrode. The reference electrode was Ag/AgCl model BJC. The solution was stirred with a rotating electrode and was kept in a thermostat at 25^{o}C. The diluter pipette model DIP-1 (Shimadzu), having 100 μL sample syringe and five continuously adjustable pipettes covering a volume range from 20 to 5000 μL (model PIPTMAN P, GILSON), were used for preparation of the experimental solutions.

Preparation of modified gold electrode

Prior to each experiment, the Au electrode was first polished, rinsed with deionized water and ultrasonicated successively in a 1:1 aqueous solution of nitric acid and an ethanol solution each for 3 min and then dried. A modified solution was prepared by putting 3 mL of DAB (2 mg.mL^{-1}) and 3 mL of Nafion–Ethanol solution (10%, v/v) in 10 mL volumetric flask, then the volume was diluted to the mark with ethanol (this solution contents 0.6mg.mL^{-1} DAB and 3%,v/v Nafion). A modified Au electrode was prepared by placing modified solution onto the dry electrode with a micro syringe. The electrode was dried to evaporate the solvent and rinsed with deionized water.

Sample preparation

A commercial formulations (as tablet) were used for the analysis of Se(IV) by using DPASVA with GEMDN. The pharmaceutical formulations were subjected to the analytical procedures:

(1) *Cenvite Silver* tablets, Pharmasyr Co., Damascus – SYRIA, Each tablet contains: 20 μg Selenium.

(2) *Cenvite* tablets, Pharmasyr Co., Damascus – SYRIA, Each tablet contains: 25 μg Selenium.

(3) *Supratech* tablets, MPI-Damascus–SYRIA, Licensed by: Roche Consumer Helth- Swizerland, Each tablet contains: 55 μg Selenium.

(4) *Selenium* tablets, Jamieson Laboratories-CANADA, Each tablet contains: 100 μg Selenium.

Three tablets of each studied pharmaceutical formulations were placed in the crucible of platinum, burning it until the flame was ended, then crushed and dissolved with 10 mL nitric acid (65%). After that, it was heated until the drought, then dissolved with $HClO_4$ solution and filtered over a 100 mL flask and diluting to 100 mL with $HClO_4$ solution. Four stock solutions of pharmaceuticals: *Cenvite Silver, Cenvite*, *Supratech* and *Selenium*, which content: 600, 750, 1650 and 3000 ng.mL^{-1} of Se(IV), respectively.

Working solutions of pharmaceuticals

These solutions were prepared by diluting: 4.167, 3.333, 1.515 and 0.833 mL of stock solutions of pharmaceuticals respectively to 100 mL with $HClO_4$ solution (each one content 25 ng.mL^{-1} selenium).

Working standard additions solutions of pharmaceuticals

These solutions were prepared as the follows: same mentioned volumes of stock solutions of pharmaceuticals with 0.000, 0.200, 0.400, 0.600 and 0.800 mL from stock solution (b) of selenium and diluting to 100 mL with $HClO_4$ solution; each one content 25 ng.mL^{-1} selenium (from pharmaceutical formulations) with 15.792, 31.584, 47.376 and 63.168 ng.mL^{-1} selenium from standard additions solutions of Se(IV), respectively.

Procedure

A 10 mL volume of a working solution containing an appropriate concentration of Se(IV) was transferred into an electrochemical cell. The accumulation potential (-200 mV) was applied to the modified electrode for a certain time. The potential was then scanned from 400 to 1250 mV by differential pulse anodic stripping voltammetry using the auto-scan facility. The peak height was measured at 980-1000 mV.

RESULTS AND DISCUSSION

Voltammetric behavior

The differential pulse anodic stripping voltammograms using the procedure described above with a bare Au electrode ($C_{Se(IV)} \geq 1x10^{-4}$ mol.L^{-1}, RSD =6.8%), while an electrode modified with DAB–Nafion shows that the peak potential shifted slightly from 980 mV to 1000 mV and the sensitivity increased ($C_{Se(IV)} \geq 5x10^{-9}$ mol.L^{-1}) when the DAB–Nafion was introduced to modify the coating (Figure 1).

Effect of modified electrode composition

The effect of the Nafion and 3,3′-Diaminobenzidine.4HCl.2H$_2$O (DAB) concentrations in modified solution for formation GEMDN on the peak current were studied. The peak current reached its maximum when the concentration Nafion is 3%,v/v and DAB is 0.6 mg.mL^{-1}.

Effect of pH

The influence of the solution $HClO_4$ (pH 0.20–1.36) was analysed with the response of the peak current. The dependence of peak

current (Ip) with pH solution was studied. Figure 2 shows that, the maximum of I_p using differential pulse anodic stripping voltammetric (DPASV) analysis for 78.96 ng.mL^{-1} of Se(IV) on DAB–Nafion modified gold electrode (GEMDN) was at pH 0.22.

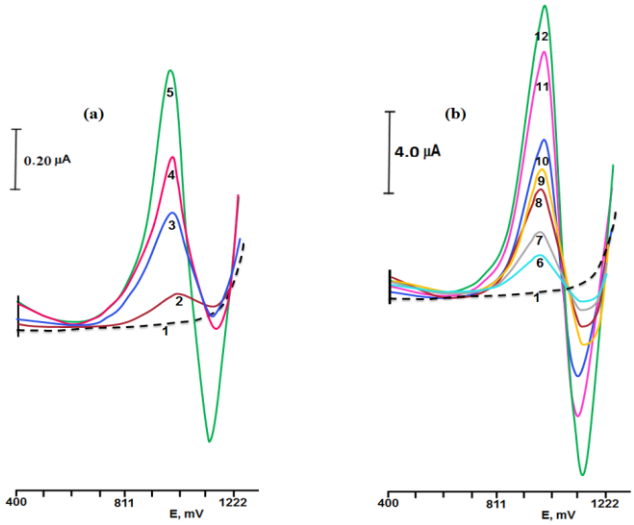


Fig.1. Differential pulse anodic stripping voltammograms of Se(IV) on DAB–Nafion modified gold electrode at pH 0.22 when $C_{Se(IV)}$: 1- electrolyte, 2- 0.3948, 3-1.974, 4- 3.948, 5- 7.896, 6- 15.792 , 7-26.283, 8-47.376, 9-63.168, 10- 78.96, 11- 118.44 and 12- 157.92 ng.mL^{-1}. (accumulation time 200 s, accumulation potential -200 mV, pH=0.22, scan rate 10 mV/s and temperature 25°± 0.5°C).

Effect of the accumulation potential

The dependence of the differential pulse anodic stripping peak current on the accumulation potential was examined. It was found that the maximum response for selenium (IV) occurs with accumulation potentials equal to -0.200 V, see Figure 3.

Effect of accumulation time

The dependence of the peak current on the accumulation time for Se(IV) concentrations was studied. The peak current increases with increasing accumulation time. The current is nearly linear from 50 to 450 s. Various parameters (electrolyte, accumulation time, accumulation potential, pH solution, scan rate, waiting time, stirring speed of electrode, initial potential, final potential and composition of modified solution) affecting the Se(IV) determination were examined. The optimum parameters for DPASV determination of selenium (IV) were selected and presented in the TABLE 1.

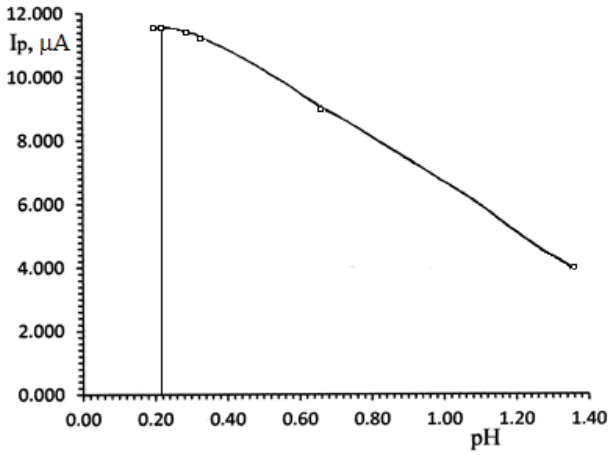


Fig. 2: Effect of pH on differential pulse anodic stripping voltammograms of Se(IV) 78.96 ng.mL^{-1} using DAB–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -200 mV, , scan rate 10 mV/s and temperature 25°± 0.5°C).

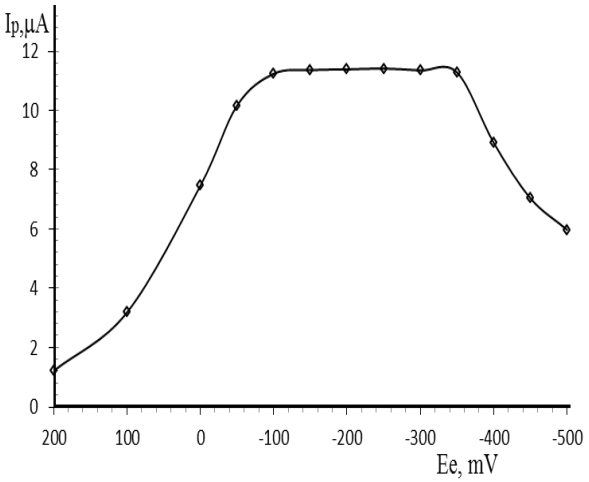


Fig. 3: Effect of accumulation potential on differential pulse anodic stripping voltammograms of Se(IV) 78.96 ng.mL^{-1} using DAB–Nafion modified gold electrode (accumulation time 200 s, pH=0.22, scan rate 10 mV/s and temperature 25°± 0.5°C)

Table 1: The optimum parameters established for differential pulse anodic stripping voltammetric determination of selenium (IV)

Parameters	Operating modes
Accumulation (deposition) time	200 s
Accumulation potential	-200 mV
Supporting electrolyte	0.20 M $HClO_4$
Indicator electrode	rotating disk gold electrode (RDGE)
pH solution	0.22
Modified electrode composition	0.6mg.mL^{-1} DAB and 3%,v/v Nafion-Ethanol
Waiting time	5 s
Initial potential	+400 mV
Final potential	+1250 mV
Scan rate	10 mV/s
Stirring speed	1000 rpm
Temperature of solution	25°± 0.5°C

Analytical results

The analytical curves, $I_p = f(C_{Se(IV)})$ for the determination of Se(IV) in presence of 0.20 M $HClO_4$ on the modified electrode (GEMDN) by DPASVA showed linear proportionality over the concentration range from 0.3948 to 157.92 ng.mL^{-1} (Figure 4). In this method we determined a very low concentration 0.3948 ng.mL^{-1} (5×10^{-9} M) of Se(IV) on the DAB–Nafion modified gold electrode in presence of 0.20 M $HClO_4$ with relative standard deviation not exceed ±4.6% (TABLE 2). This method gives accurate and sensitive results compared with obtained results using bare gold electrode; the sensitivity was increased about 20000 times.

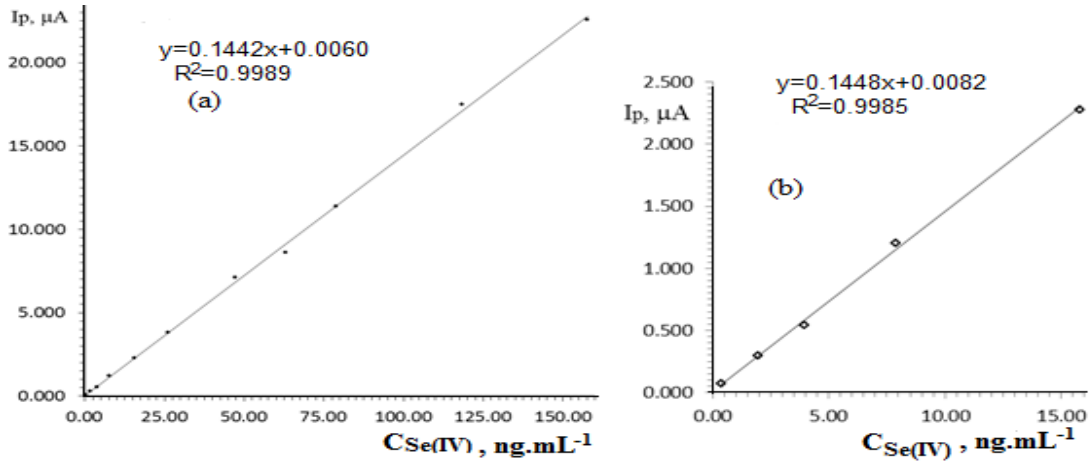


Fig. 4: $I_p = f(C_{Se(IV)})$ for the determination of Se(IV) in presence of 0.20 M $HClO_4$ by DPASVA using a DAB–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -200 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C and n=5; y: I_p, µA and x: $C_{Se(IV)}$, ng.mL^{-1}).

Table 2: Determination of selenium(IV) by DPASVA on a DAB–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -200 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C and n=5, t=2.776).

x_i, ng.mL^{-1} (taken)	$\bar{x}$, ng.mL^{-1} (found)	SD, ng.mL^{-1}	$\frac{SD}{\sqrt{n}}$, ng.mL^{-1}	$\bar{x} \pm \frac{t.SD}{\sqrt{n}}$, ng.mL^{-1}	RSD %
0.3948	0.414	0.002	0.0085	0.414 ± 0.024	4.6
1.974	1.974	0.087	0.039	1.974 ± 0.108	4.4
3.948	3.673	0.154	0.069	3.673 ± 0.191	4.2
7.896	8.231	0.337	0.151	8.231± 0.419	4.1
15.792	15.69	0.628	0.281	15.69 ± 0.780	4.0
26.283	26.28	1.05	0.47	26.28 ± 1.30	4.0
47.376	49.20	1.92	0.86	49.20 ± 2.38	3.9
63.168	59.60	2.20	0.99	59.60 ± 2.74	3.7
78.96	79.02	2.76	1.24	79.02 ± 3.43	3.5
118.44	121.32	4.00	1.79	121.32 ± 4.97	3.3
157.92	156.68	4.70	2.10	156.68 ± 5.83	3.0

Table 3: Regression equations and correlation coefficients for determination of $C_{Se(IV)}$ in pharmaceutical preparations using DPASV on a DAB–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -200 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C and n=5).

Pharmaceutical preparations	$C_{Se(IV)}$ in tab., µg	Operating modes			
		Regression equations*	Correlation coefficients	m', ng.mL^{-1}	Amount of Se^{4+} (m), µg/tab.
Cenvite Silver tablets, Pharmasyr Co., Damascus – SYRIA	20	y=0.1443x+3.569	R^2=0.9984	24.733	m =0.8m'=19.786
Cenvite tablets, Pharmasyr Co., Damascus – SYRIA	25	y=0.1440x+3.620	R^2=0.9989	25.139	m =1.0m'=25.139
Supratech tablets, MPI-Damascus–SYRIA, Licensed by: Roche Consumer Helth- SWIZERLAND	55	y=0.1446x+3.752	R^2=0.9986	25.947	m =2.2m'=57.083
Selenium tablets, Jamieson Laboratories, CANADA	100	y=0.1442x+3.682	R^2=0.9992	25.534	m =4.0m'=102.14

*y= n A, x= $C_{Se(IV)}$ (ng.mL^{-1})= m' = intercept/slope.

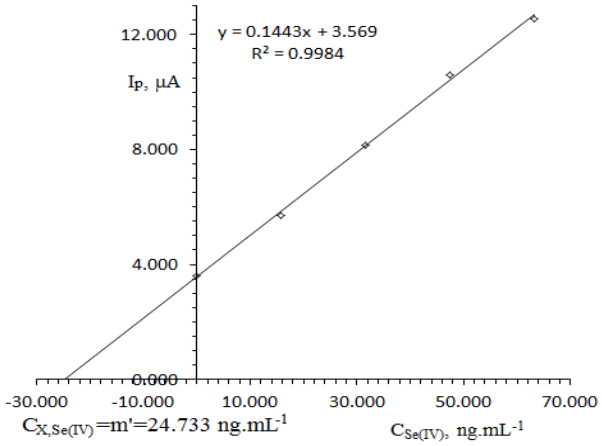


Fig. 5: The standard addition curve for determination of Se(IV) in *Cenvite Silver* (20 µg/tab.)using DPASV on a DAB–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -200 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C and n=5).

Applications

Many applications for the determination of Se(IV) in some pharmaceutical preparations by DPASVA on a DAB–Nafion modified gold electrode using the optimum parameters were proposed. Standard addition curves for determination of Se(IV) in different pharmaceutical preparations (*Cenvite Silver*, *Cenvite*, *Supratech* and *Selenium*) were used. The standard addition curve of *Cenvite Silver* (20 µg/tab.) was showed in Figure 5, as an example. Regression equations and correlation coefficients were included in Table 3. Standard addition curves for determination of Se(IV) in different pharmaceutical preparations were used .

The amount (m) of Se(IV) in one tablet by µg/tab calculated from the following relationship: m = h. m', where: m' is the amount of Se(IV) in tablet, which calculated from the standard additions curve according to the following regression equation: y=a.x+b; when y=0; m'=x= b/a= intercept/slope (ng.mL^{-1}) and h conversion factor is equal to 0.8, 1.0, 2.2 and 4.0 for all pharmaceuticals content 20, 25, 55 and 100 µg/tab, respectively. The results of quantitative analysis for Se(IV) in the pharmaceutical preparations using this method were included in Table 4. The proposed method was simple, economic, accurate and successfully applied to the determination of Se(IV) in pharmaceuticals. The results obtained agree well with the contents stated on the labels.

Table 4: Determination of Se(IV) in pharmaceutical preparations using DPASV on a DAB–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -200 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C and n=5).

Commercial name	Contents, µg/tab.	$\bar{x}$, µg/tab.	RSD%	Recovery %
Cenvite Silver tablets, Pharmasyr Co., Damascus – SYRIA	20	19.786	4.5	98.93
Cenvite tablets, Pharmasyr Co., Damascus – SYRIA	25	25.139	4.4	100.56
Supratech tablets, MPI-Damascus–SYRIA	55	56.247	4.2	103.79
Selenium tablets, Jamieson Laboratories, CANADA	100	104.96	4.1	102.14

CONCLUSION

Differential pulse anodic stripping voltammetric Analysis (DPASVA) of selenium(IV) using a gold electrode modified with 3,3′-diaminobenzidine.4HCl-nafion (GEMDN) has been studied. Selenium(IV) was determined in an aqueous $HClO_4$ (0.2M) medium of pH 0.22. Under the optimum conditions, liner calibration graph, $I_p=f(C_{Se4}+)$, was obtained in the concentration ranges of 0.3948 to 157.92 ng.mL^{-1} with relative standard deviations (RSD) $\leq$ 4.6%, and the detection limit 0.06 ng.mL^{-1}. This method showed a good accumulation efficiency for selenium and good resistance to interferences from metal ions as well as those associated with selenium in pharmaceuticals. The results for the determination of Se^{4+} using GEMDN were more sensitive and accurate than that obtained using bare gold electrode; the sensitivity was increased about 20000 times.

REFERENCES

1. Mi-Sook Won, Jang-Hee Yoon, Yoon-Bo Shim, Determination of Selenium with a Poly(1,8-diamino-naphthalene)-Modified Electrode. *Electroanalysis*, 2005; 17(21):1952-1958.
2. STOICA AI, BABAUA G, IORGULESCU EE, MARINESCU D, BAIULESCU GE, Differrential Pulse cathodic stripping voltammetric determination of selenium in pharmaceutical products, *J Pharm Biomed Anal*, 2002; 30:1425-1429.
3. Soo Beng Khoo, Ruidong Ye, Differential pulse voltammetric determination of trace Te(IV) at a poly(3,3′-diaminobenzidine) film modified gold electrode in flow systems, *Anal Chim Acta*, 2002;453(2):209–220.
4. Hao-Yun Yang, I-Wen Sun, Cathodic stripping voltammetric determination selenium(IV) at a nafion coated mercury film electrode modified with 3,3'-diaminobenzidine. *Electroanalysis*, 2000; 12:1476-1480.
5. Ramadan AA, Mandil H, Ozoun A, Determination of Se(IV) by Pulse Anodic Stripping Voltammetry with a Vitamin E – Nafion Modified Gold Electrode. *Res J of Aleppo Univ,* Syria, 2008; 61:149- 184.
6. Ramadan AA, Mandil H, Ozoun A, Differential pulse anodic stripping voltammetric determination of selenium(IV) with a vitamin e–nafion modified gold electrode. *Asian J Chem*, 2011; 23:843-846.
7. Ramadan AA, Mandil H, Ozoun A, Determination of se (IV) in pharmaceuticals by using different operating modes of pulse anodic stripping voltammetric analysis with a methylene blue-nafion modified gold electrode. *Asian J Chem*, 2013; 24(4):3393-3397.
8. Ramadan AA, Mandil H, Ozoun A, Differential pulse anodic stripping voltammetric determination of selenium(IV) with a methylene blue-nafion modified gold electrode. *Asian J Chem*, 2012; 24: 391-394.
9. Ramadan AA, Mandil H, Hafez B, Differential pulse polarographic determination of atorvastatin in pharmaceutical dosage forms using dropping mercury electrode, *Asian J Chem*, 2013; 25 (6): 3467-3472.
10. Ramadan AA, Mandil H, Hafez B, Differential pulse polarography of atorvastatin in pure and pharmaceutical dosage forms using static mercury drop electrode, *Int J Pharm Pharm Sci*, 2013; 5 (1): 434-440.
11. Ramadan AA, Mandil H, Hafez B, Effect of hanging mercury drop electrodeon differential pulse polarographic analysis of atorvastatin in pharmaceuticals using borax buffer at pH7.50, *Int J Pharm Pharm Sci*, 2012; 4 (SUPPL. 5): 540-546.

12. Ramadan AA, Mandil H, Determination of gatifloxacin in pure form and pharmaceutical formulations by differential pulse polarographic analysis, *Anal Biochem*, 2010; 404: 1-7.
13. Ramadan AA, Mandil H, Genco T, Determination of carbinoxamine maleate in pharmaceuticals by direct and differential pulse polarography, *Asian J Chem*, 2009; 21(9):7387-7397.
14. Ramadan AA, Mandil H,, Hafez B, Determination of dipyrone in pure form and pharmaceutical formulations by differential pulse polarographic analysis, *Asian J Chem*, 2011; 21(1):403-406.
15. Ramadan AA, Mandil H, Determination of lomefloxacin in pharmaceuticals using differential pulse polarographic analysis, *Int J Pharm Pharm Sci*, 2012; 4 (SUPPL. 5): 255-261.