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Original Article

DEVELOPMENT AND VALIDATION OF DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRIC ANALYSIS OF SELENIUM (IV) IN BULK AND IN DOSAGE FORMULATIONS AT A GOLD ELECTRODE MULTI-MODIFIED WITH A MIXTURE OF 3, 3′-DIAMINOBENZIDINE.4HCL AND VITAMIN E

ABDUL AZIZ RAMADAN*, HASNA MANDIL, ABDULRAHMAN SHIKH-DEBES

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

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ABSTRACT

Objective: A simple, direct and very sensitive differential pulse anodic stripping voltammetric analysis (DPASVA) of selenium (IV) in bulk and in dosage formulations using a gold electrode multi-modified with a mixture of 3,3′-diaminobenzidine.4HCl (D_{ab}) and vitamin E (V_E)-Nafion ($AuEMD_{ab}V_EN$) has been studied.

Methods: The method involves the study of various parameters (electrolyte, deposition time, pulse duration, pulse amplitude, etc.) affecting the Se(IV) determination. The proposed method was validated for specificity, linearity, precision and accuracy, repeatability, sensitivity (LOD and LOQ), robustness and solution stability with an average recovery of 98.1-100.32%.

Results: Se(IV)was determined in an aqueous $HClO_4$ (0.2M) medium of pH 0.22 at an accumulation potential of-250 mV and an accumulation time of 200 s for $C_{Se(IV)}$ at $1x10^{-8}$ to $1x10^{-6}$ mol/l (0.7896-78.96 ng/ml) and 350 s for $C_{Se(IV)}$ at $1x10^{-9}$ to $1x10^{-8}$ mol/l (0.07896-0.7896 ng/ml) with relative standard deviations (RSD)$\leq$2.4% and 4.8%, respectively.

Conclusion: This method showed very sensitive results for the determination of Se(IV) using an $AuEMD_{ab}V_EN$ than that obtained using the individual D_{ab} or V_E. This method could be applicable for the quantitative determination of the bulk Se(IV) as well as dosage formulations.

Keywords: Multi-Modified, Vitamin E, 3,3′-Diaminobenzidine.4HCl, Nafion, Se(IV), Differential pulse anodic stripping voltammetry

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INTRODUCTION

Electrochemical sensor based on gold nanoparticle (AuNP) modified glassy carbon electrode for the determination of the Se in water to the limit of 0.64 µg/l using square wave anodic stripping voltammetry (ASV)was studied [1]. A procedure of Se(IV) determination by ASV using two deposition and stripping steps at gold electrodes was proposed. A linear relationship was observed in the range from 5×10^{-9} to 1×10^{-7} mol/l [2]. A new, simple, and reproducible method is described for the determination of Se (IV) based on differential pulse cathodic stripping voltammetry (DPCSV). The calibration graph is linear up to at least 40 ng/ml of Se(IV) with a relative standard deviation (RSD%) of 2.7% for 20 ng/ml (n=5) [3]. Electrochemical sensor with the renewable silver annular band working electrode and its application for cathodic stripping voltammetric determination of Se(IV) in real water samples was applied [4]. The performance of a poly(1,8-diaminonaphthalene)-modified gold electrode for the determination of the Se(IV) ion in an aqueous medium was investigated with anodic stripping voltammetry. The detection limit employing the anodic stripping differential pulse voltammetry was 9.0 $x10^{-9}$ M for Se(IV) with 4.4 % of RSD% [5]. DPCSV determination of Se (IV) from pharmaceutical products was applied. The Se was determined in the range 8 to 64 ng/ml in pharmaceutical products [6]. Electro polymerization of 3,3′-diaminobenzidine (D_{ab}) on a gold surface gave an adherent, stable film of poly(3,3′-diaminobenzidine). The optimized method for the continuous flow mode had a detection limit of 5.6×10^{-9} mol/l of Te(IV) for 10 min preconcentration [7]. Determination of Se(IV) was investigated on 3,3'-diaminobenzidine/ Nafion/mercury film modified glass carbon electrode. The analytical signal using cathodic square wave stripping voltammetry (SWSV) was linear from 1 to 300 µg/l with 5 min accumulation [8]. Determination of $Se^{4+}$by pulse anodic stripping voltammetry with constant amplitude of negative polarity [9] and differential pulse anodic stripping voltammetric analysis (DPASVA) [10] using a Vitamin E–Nafion modified gold electrode in a aqueous $HClO_4$ medium (pH=1.1) at an accumulation potential (P_{ac}) of-240 mV and an accumulation time (t_{ac}) of 300 s has been studied. The analytical signal was linear from in the concentration ranges of $1x10^{-7}$ to $8x10^{-6}$ mol/l with RSD% $\leq$5.2% [9] and 5×10^{-8} to 1×10^{-5} mol/l with RSD% 4.5 % [10]. Determination of Se(IV) in Syrian pharmaceuticals with a methylene blue-Nafion modified gold electrode by using different operating modes of pulse anodic stripping voltammetry: with a constant amplitude of negative or positive polarity, imposed pulses of linearly increasing amplitude and differential sampling on successive pulses ($\Delta I/\Delta t$) was applied. The methods were applied to the determination of Se(IV) in Syrian pharmaceuticals with high sensitivity and accuracy[11]. DPASVA of Se(IV) using a methylene blue-Nafion modified gold electrode (MBNMAuE) has been studied. The calibration graph for Se(IV) was linear in the range from 1×10^{-8} to 1×10^{-6} mol/l (0.79 ng/ml to 79 ng/ml) [12]. DPASVA of Se(IV) using a gold electrode modified with D_{ab}-Nafion ($AuEMD_{ab}N$) has been applied. Se(IV)was determined in an aqueous $HClO_4$ (0.2M) medium of pH 0.22 at a P_{ac} of-200 mV and a t_{ac} of 200 s. Liner calibration curve was obtained in the concentration ranges of $5x10^{-9}$ M to $2x10^{-6}$ M with RSD% $\leq$4.6% [13].

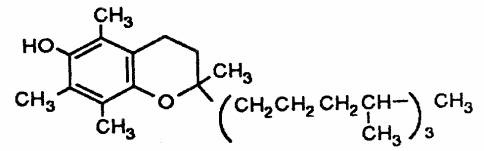
In the present work, Differential pulse anodic stripping voltammetric analysis (DPASVA) of Se(IV) using an $AuEMD_{ab}V_EN$ has been applied. This method showed very sensitive results for the determination of Se(IV) than that obtained using the individual D_{ab} or V_E. This method could be applicable for the quantitative determination of the bulk Se(IV) as well as dosage formulation.

MATERIALS AND METHODS

Chemicals

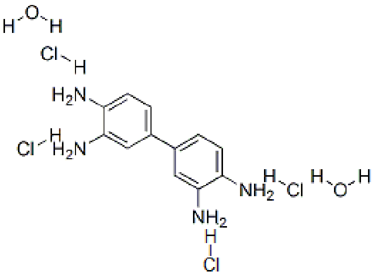
Nafion perfluorinated ion-exchange resin in ethanol (3%, v/v) was purchased from Aldrich. Vitamin E, molecular weight 430.72 g/mol (Scheme 1) was from Basf/Germany. 3,3′-diaminobenzidine.

$4HCl.2H_2O$, molecular weight 396.2 g/l (Scheme2) was from SERVA Electrophoresis Gmbh (Purity 96.0%). H_2SeO_3 and all other reagents were of analytical grade from Merck.



Scheme 1: Vitamin E(DL-α-tocopherol), $C_{29}H_{50}O_2$, V_E

A stock solutions (a) and (b) of Se(IV) 789.6 µg/ml (0.01 mol/l) and 7.896 µg/ml (0.1 mmol/l) were prepared using $HClO_4$ solution 0.20M (pH=0.22). All working solution for voltammetric investigations was prepared by dilution of the stock solutions of Se(IV) (a or b) with $HClO_4$ solution.



Scheme 2: 3,3′-Diaminobenzidine.$4HCl.2H_2O$, $C_{12}H_{14}N_4 \cdot 4HCl \cdot 2H_2O$, D_{ab}

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 °C. The diluter pipette model DIP-1 (Shimadzu), having 100 µL sample syringe and five continuously adjustable pipettes covering a volume range from 5 to 5000 µL (model PIPTMAN P, GILSON), were used for preparation of the experimental solutions.

Preparation of modified gold electrode

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 3.15 ml of D_{ab} (2 mg/ml), 3.0 ml of V_E (1 mg/ml), 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 0.63 mg/ml D_{ab}, 0.30 mg/ml V_E and3%,v/v Nafion). A multi-modified Au electrode was prepared by placing (5 µl) modified solution onto the dry electrode with a micro syringe. The electrode was dried to evaporate the solvent and rinsed with deionized water ($AuEMD_{ab}V_EN$).

Sample preparation

Commercial formulations (as a tablet) were used for the analysis of Se(IV) by using DPASVA with $AuEMD_{ab}V_EN$. The pharmaceutical formulations were subjected to the analytical procedures:

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

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

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

Twenty tablets of each studied pharmaceutical formulations were placed in the crucible of platinum, burning it until the flame was ended, crushed to a fine powder mixed well and weighted. An amount of the powder equivalent to the weight of one tablet was solved 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. Three stock solutions of pharmaceuticals were prepared {Selenium, Cenvite and Supratech, which content: 1000, 250 and 550 ng/ml of Se(IV), respectively}.

Working solutions of pharmaceuticals

These solutions were prepared by diluting: 2.500, 10.000 and 4.545 ml of stock solutions of pharmaceuticals respectively to 100 ml with $HClO_4$ solution (each one content 25 ng/ml Se).

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 Se and diluting to 100 ml with $HClO_4$ solution; each one content 25 ng/ml Se (from pharmaceutical formulations) with 15.792, 31.584, 47.376 and 63.168 ng/ml Se 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 (-250 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 voltammetric analysis using the auto-scan facility. The peak height was measured at 995-1010 mV.

RESULTS AND DISCUSSION

Voltammetric behavior

The differential pulse anodic stripping voltammograms using the procedure described above with an electrode multi-modified with a mixture of (D_{ab} and V_E)–Nafion shows that the peak potential shifted slightly from 995 mV to 1010 mV and the sensitivity increased ($C_{Se(IV)} \geq 1x10^{-9}$ mol/l). While the sensitivity by using modified electrode with D_{ab} or V_E only not reached less than $5x10^{-9}$ mol/l.

Effect of pH solution

Effect of pH on differential pulse anodic stripping voltammograms of Se(IV) using $AuEMD_{ab}V_EN$ was studied. It was found that the best pH solution 0.22.

Effect of modified electrode composition

The effect of the Nafion, D_{ab} and V_E concentrations in modified solution for formation $AuEMD_{ab}V_EN$ on the peak current were studied. The peak current reached its maximum when the concentrations of Nafion, D_{ab} and V_E were 3%v/v, 0.63 mg/ml and 0.30 mg/ml, respectively.

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 Se (IV) occurs with accumulation potentials equal to-0.250 V.

Effect of accumulation time (t_a)

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. The best time was 200 s for Se(IV) concentrations $1x10^{-8}$-$1x10^{-6}$ mol/l and 350 s for Se(IV) concentrations $1x10^{-9}$-$1x10^{-8}$

mol/l. 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 Se (IV) were selected and presented in the table 1.

Table 1: The optimum parameters established for differential pulse anodic stripping voltammetric determination of Se (IV) using an AuEMD$_{ab}$V$_E$N

Parameters	Operating modes
Accumulation (deposition) time (t_{ac})	200 s for $C_{Se(IV)}$ $1x10^{-8}$-$1x10^{-6}$ mol/l and 350 s for $C_{Se\ (IV)}$ $1x10^{-9}$-$1x10^{-8}$ mol/l
Accumulation potential (P_{ac})	-250 mV
Supporting electrolyte	0.20 M $HClO_4$
Indicator electrode	rotating disk gold electrode (RDAuE)
pH solution	0.22
Modified electrode composition	0.63 mg/ml of D_{ab}+0.30 mg/ml of V_E+3%,v/v Nafion in Ethanol
Drop modified size	5µl
Initial potential	+400 mV
Final potential	+1250 mV
Peak potenthial	995-1010 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 $HClO_4$ using a AuEMD$_{ab}$V$_E$N by DPASVA showed linear proportionality over the concentration range from 0.07896 ng/ml (1×10^{-9} mol/l) to 0.7896 ng/ml ($1x10^{-8}$ mol/l) of Se(IV) with accumulation (deposition) time 350 s and 0.7896 ng/ml ($1x10^{-8}$ mol/l) to 78.96 ng/ml ($1x10^{-6}$ mol/l) of Se(IV) with accumulation time 200 s (fig. 1 and 2). Regression equations and correlation coefficient were as the follows: y=1.6415x+0.0353 (R^2=0.9973) and y=0.3178x+0.0598 (R^2=0.9995), respectively. In this method a very low concentration 0.07896 ng/ml (1×10^{-9} mol/l) of Se(IV) with relative standard deviation not exceed±4.8% was determined (table 2).

This method showed a very sensitive results for the determination of Se(IV) than that obtained using D_{ab} or V_E modified gold electrode [10, 13]; because the effect of multi-modified a gold electrode with a mixture of D_{ab} and V_E-Nafion making the electrode is more selective for Se (IV) compared to the modified electrode with the individual D_{ab} 10 or V_E 13-Nafion.

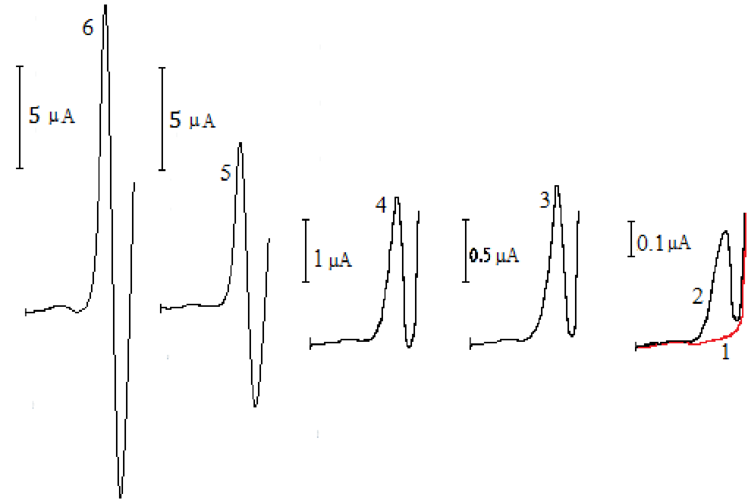


Fig. 1: Determination of Se(IV) in presence of 0.20 M $HClO_4$ by DPASVA using a AuEMD$_{ab}$V$_E$N when $C_{Se(IV)}$: 1-electrolyte, 2-0.7896, 3-3.948, 4-7.896, 5-39.480 and 6-78.960 ng/ml (t_{ac} 200s, P_{ac}-250 mV, pH=0.22, scan rate 10 mV/s, temperature 25 °±0.5 °C, n=5)

APPLICATIONS

Many applications for the determination of Se(IV) in some pharmaceutical preparations by DPASVA on an AuEMD$_{ab}$V$_E$N using the optimum parameters were proposed. Standard addition curves for determination of Se(IV) in different pharmaceutical preparations (Cenvite, Supratech and Se) were used. 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 mg/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) and h conversion factor is equal to 1.0, 2.2 and 4.0 for all pharmaceuticals content 25, 55 and 100 µg/tab, respectively. The results of the quantitative analysis for Se(IV) in the pharmaceutical preparations using this method included in table 4. The proposed method was simple, very sensitive and successfully applied to the determination of Se(IV) in pharmaceuticals. The results obtained agree well with the contents stated on the labels.

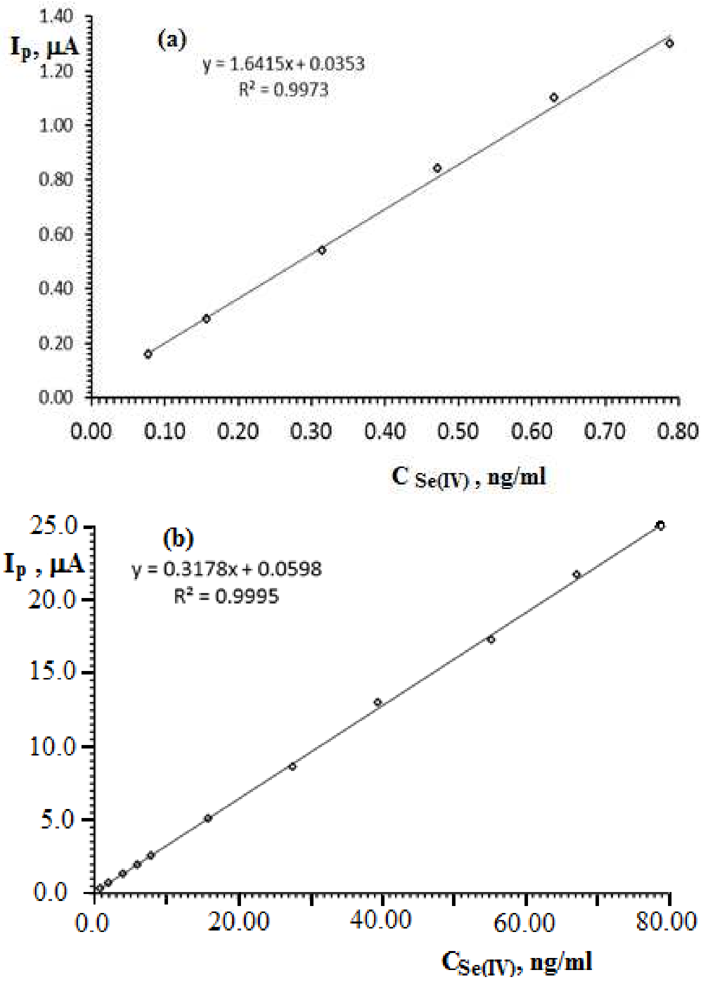


Fig. 2: I_p = f ($C_{Se(IV)}$) for the determination of Se(IV) in presence of 0.20 M $HClO_4$ by DPASVA using a $AuEMD_{ab}V_EN$ (t_{ac} 350 s (a) and 200 s (b), P_{ac}-250 mV, pH=0.22, scan rate 10 mV/s, temperature 25 °±0.5 °C, n=5; y: I_p, μA and x: $C_{Se(IV)}$, ng/ml)

Table 2: Determination of Se(IV) by DPASVA on a $AuEMD_{ab}V_EN$ (t_{ac}: 350 s for $C_{Se(IV)}$ 0.07896-0.7896 ng/ml and 200 s for $C_{Se(IV)}$ 0.7896-78.96 ng/ml, a P_{ac}**-250 mV, pH=0.22, scan rate 10 mV/s, temperature 25 °±0.5 °C, n=5 and t=2.776)**

x_i, ng. ml^{-1} (taken)	t_{ac}, s	$\overline{x}$ ±SD, ng/ml (found)	$\frac{SD}{\sqrt{n}}$, ng/ml	$\bar{x} \pm \frac{t.SD}{\sqrt{n}}$, ng/ml	RSD %	$\overline{X}$ ±SD, ng/ml (found [13])
0.07896	350	0.0772±0.0062	0.0017	0.0772±0.0046	4.8	Not determined
0.15792		0.1552±0.0073	0.0033	0.1552±0.0091	4.7	=
0.31584		0.3075±0.014	0.0063	0.3075±0.017	4.7	=
0.47376		0.4902±0.023	0.0103	0.4902±0.029	4.6	0.4873±0.023
0.63168		0.6486±0.029	0.0130	0.6486±0.036	4.5	0.6326±0.029
0.78960		0.7705±0.034	0.0152	0.7705±0.042	4.4	0.7800±0.034
0.7896	200	0.803±0.034	0.0152	0.803±0.042	4.2	0.7692±0.034
1.974		2.014±0.082	0.037	2.014±0.103	4.1	1.997±0.086
3.948		3.902±0.153	0.068	3.902±0.189	3.9	3.950±0.155
5.922		5.948±0.226	0.101	5.948±0.281	3.8	5.989±0.236
7.896		7.836±0.290	0.130	7.836±0.360	3.7	7.830±0.337
15.792		15.860±0.587	0.263	15.860±0.730	3.7	15.902±0.627
27.636		26.873±0.967	0.432	26.873±1.200	3.6	26.897±1.02
39.480		40.718±1.47	0.657	40.718±1.825	3.6	40.248±1.83
55.292		54.249±1.90	0.849	54.249±2.357	3.5	55.250±1.90
67.116		68.093±2.38	1.066	68.093±2.959	3.5	68.022±2.32
78.960		78.478±2.75	1.228	78.478±3.410	3.5	78.034±2.76

Validation of proposed method

The developed method for simultaneous estimation of Se(IV) has been validated in accordance with the International Conference on Harmonization guidelines (ICH) [14].

Selectivity

Selectivity test determines the effect of excipients on the assay result. To determine the selectivity of the method, a standard solution of Se(IV), commercial product solution and blank solutions were analyzed. The results of the tests proved that the effect of the presence of common excipients such as; starch, lactose, glucose, sucrose, and gum acacia no interference was introduced by any of them.

Table 3: Regression equations and correlation coefficients for determination of $C_{Se(IV)}$ in pharmaceutical preparations using DPASV on a AuEMD$_{ab}$V$_E$N (t_{ac} 200 s, P_{ac}-250 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	Amount of Se^{4+}(m), µg/tab.
Cenvite tablets, Pharmasyr Co., Damascus–SYRIA	25	y=0.3180x+7.950	R^2=0.9989	25.00	m =1.0m'=25.00
Supratech tablets**,** MPI-Damascus–SYRIA, Licensed by: Roche Consumer Helth-SWIZERLAND	55	y=0.3164x+7.973	R^2=0.9986	25.20	m =2.2m'=55.44
Se tablets, Jamieson Laboratories, CANADA	100	y=0.3214x+8.061	R^2=0.9992	25.08	m =4.0m'=100.32

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

Table 4: Determination of Se(IV) in pharmaceutical preparations using DPASV on a AuEMD$_{ab}$V$_E$N (t_{ac} 200 s, P_{ac}-200 mV, pH=0.22, scan rate 10 mV/s, temperature 25 °±0.5 °C and n=5)

Commercial name	Contents, µg/tab.	$\bar{X}$ ±SD, µg/tab.	RSD%	Assay %
Cenvite tablets, Pharmasyr Co., Damascus–SYRIA	25	25.00±1.00	4.0	100.00
Supratech tablets, MPI-Damascus–SYRIA	55	55.44±2.16	3.9	100.80
Se tablets, Jamieson Laboratories, CANADA	100	100.32±3.81	3.8	100.32

Linearity

In the proposed methods, linear plots (n= 5) with good correlation coefficients were obtained in the concentration ranges of 0.07896–0.78960 and 0.78960-78.960 ng/ml for Se(IV), linearity equations obtained were y=1.6415x+0.0353 (R^2=0.9973) and y=0.3178x +0.0598 (R^2=0.9995) using accumulation time 350 s and 200 s, respectively.

Precision and accuracy

The precision and accuracy of proposed method were checked by recovery study by addition of standard Se(IV) solution to pre-analyzed sample solution at three different concentration levels (80%, 100% and 120%) within the range of linearity for Se(IV). The basic concentration level of sample solution selected for spiking of the Se(IV) standard solution was 27.636 ng/ml. The proposed method was validated statistically and through recovery studies and was successfully applied for the determination of Se(IV) in pure and dosage forms with percent recoveries ranged from 98.0% to 101.0% (table 5).

Repeatability

The repeatability was evaluated by performing 10 repeat measurements for 7.896 ng/ml of Se(IV) using the studied method under the optimum conditions in two concentration ranges. The found amount of Se(IV) ($\bar{X}$ ±SD) was 7.836±0.29 ng/ml and the percentage recovery was found to be 99.24±3.67 with RSD of 0.037. These values indicate that the proposed method has high repeatability for Se(IV) analysis.

Table 5: Results of recovery studies (n=5)

Level	% recovery
80%	98.0
100%	100.2
120%	101.0

Table 6: Robustness of the proposed DPASVA method

Experimental parameter variation	Average recovery (%)*
	$C_{Se(IV)}$=27.636 ng/ml
Temperature	
15 °C	99.9
25 °C	100.1
pH	
0.21	99.8
0.23	99.7
Accumulation potential	
-245 mV	100.2
-255 mV	100.1
C_{HClO4}	
0.19 mol/l	99.7
0.21 mol/l	99.9

* n=5.

Sensitivity (LOD and LOQ)

The limits of detection (LOD) and quantitation (LOQ) were determined using the formula: LOD or LOQ =jSD/b, where j =3.3 for LOD and 10 for LOQ, SD is the standard deviation of the intercept, and b is the slope. The values of LOD and LOQ for Se(IV) are 0.0075 and 0.023, respectively.

Robustness

The robustness of the method adopted is demonstrated by the constancy of the current peak (I_P) with the deliberated minor change in the experimental parameters such as the change in the concentration of excipients, temperature (25±5 °C), pH (0.22±0.01), accumulation potential (-250±5 mV) and C_{HClO4} (0.20±0.01 mol/l), table 6 indicates the robustness of the proposed method. I_p was measured and the assay was calculated for five times.

Specificity

The specificity of the method was ascertained by analyzing standard Se(IV) in presence of excipients. There was no interference from the common excipients.

CONCLUSION

Differential pulse anodic stripping voltammetric analysis (DPASVA) of Se(IV) using $AuEMD_{ab}V_EN$ has been studied. Se(IV)was determined in an aqueous $HClO_4$ (0.2M) medium of pH 0.22. Under the optimum conditions this method showed that the effect of multi-modified of gold electrode with a mixture of D_{ab} and V_E-Nafion making the electrode is more selective for Se (IV) compared to the modified electrode with the individual D_{ab} [10] or V_E [13]-Nafion

CONFLICT OF INTERESTS

The authors declare no conflict of interest

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