Differential Pulse Anodic Stripping Voltammetric Determination of Selenium (IV) in Bulk and in Dosage Formulations Using a Gold Electrode Modified with a Mixture of o-Phenylenediamine and 2,3-Diaminonapthhalene-Nafion

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ABSTRACT

The effect of gold electrode modified with 2,3-Diaminonaphthalene ($GEM_{DAN}N$) or multi-modified or a mixture 2,3-diaminonaphthalene and o-phenylenediamine -nafion ($GEM_{DAN-OPDA}N$) on determination of selenium (IV) using differential pulse anodic stripping voltammetric analysis (DPASVA) has been studied. Various parameters (electrolyte, deposition time, pulse duration, pulse amplitude, etc.) are affecting determination of the Se (IV) in $HClO_4$ (0.2 M) at pH 0.22 were examined. Under the optimum conditions, calibration graph, $I_p=f(C_{Se(IV)})$, were obtained in the concentration ranges of $5x10^{-8}$ - $1x10^{-6}$ M (3.948 -78.96 $ng.mL^{-1}$) with relative standard deviations (RSD) ≤ 4.2% and detection limit 0.056 $ng.mL^{-1}$, and $1x10^{-9}$ -$1x10^{-6}$ M (0.07896 -78.96 $ng.mL^{-1}$) with relative standard deviations (RSD) ≤ 4.9% and detection limit was 0.014 $ng.mL^{-1}$ on $GEM_{DAN}N$ and $GEM_{DAN-OPDA}N$, respectively. 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 (IV) using $GEM_{DAN-OPDA}N$ (multi-modified) were more sensitive (about 50 times) than that obtained using $GEM_{DAN}N$.

Keywords: Multi-modified, 2,3-Diaminonaphthalene, o-Phenylenediamine, Nafion, Selenium (IV), Differential pulse anodic stripping voltammetry.

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1. 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 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} M for 10 min preconcentration [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. Se (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 $\mu g.L^{-1}$ with 5 min accumulation [4].

Differential pulse anodic stripping voltammetric analysis of selenium (IV) using a gold electrode modified with 3,3′-diaminobenzidine.4HCl-nafion (GEMDN) has been studied. Selenium (IV) was determined. Liner calibration graph was obtained in the concentration ranges of $5x10^{-9}$ M to $2x10^{-6}$ M with RSD$\leq$4.6% [5].

DPASVA of selenium (IV) using a gold electrode modified with o-Phenylenediamine-nafion has been studied. Liner calibration graph, $I_p=f(C_{Se^{4+}})$, was obtained in the concentration ranges of 3.948 to 78.96 $ng.mL^{-1}$ with relative standard deviations (RSD)$\leq$3.8%, and the detection limit was 0.048 $ng.mL^{-1}$ [6].

Differential pulse anodic stripping voltammetric determination of selenium (IV) using a vitamin E-nafion modified gold electrode has been studied. Selenium (IV) was determined. Liner calibration graph was obtained in the concentration ranges of 5×10^{-8} - 1×10^{-5} M with relative standard deviations (RSD) 4.5 % [7].

A simple, direct and very sensitive DPASVA of selenium (IV) in bulk and in dosage formulations using a gold electrode multi-modified with a mixture of {3,3′-diaminobenzidine.4HCl and vitamin E (V_E) –nafion} (GEMDV$_E$N) has been studied. Liner calibration graph was obtained in the concentration ranges of 1×10^{-9} - 1×10^{-6} M with relative standard deviations (RSD) 4.8 % [8].

Many spectrophotometric methods for the determination of selenium have been reported with some chromogenic reagents, such as 3,3-diaminobenzidine tetrahydrochloride], 2,3-diaminonaphthalene, 2-mercapto benzothiazole, o-phenylenediamine], dithizone], 8-hydroxyquinoline, leuco crystal violet, variamine blue], methylene blue, and iodide [9-12].

Atomic absorption spectrometry methods for the determination of selenium with continuous-flow hydride generation electrothermal atomic absorption spectrometry with in situ trapping on an iridium-coated graphite tube has been chosen because of the high sensitivity and relative simplicity [13-16].

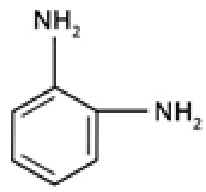
In the present work, the effect of gold electrode modified with GEM$_{DAN}$N and gold electrode multi-modified with a mixture o-phenylenediamine and 2,3-diaminonaphthalene-nafion on determination of selenium (IV) using differential pulse anodic stripping voltammetric analysis has been studied.

2. EXPERIMENTAL

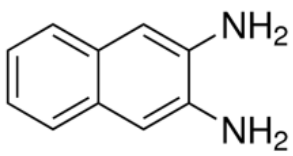
2.1 Reagents

Nafion perfluorinated ion-exchange resin in ethanol (3%, v/v) was purchased from Aldrich. O-Phenylenediamine, mol. mass 108.144 g/mol (Scheme 1) were of analytical grade from Merck. 2,3-Diaminonaphthalene, molecular weight 158.2 g/mol (Scheme 2) was from Aldrich. H_2SeO_3 and all other reagents were of analytical grade from Merck.

Scheme 1: O-Phenylenediamine, ($C_6H_8N_2$) or O-PDA



Scheme 2: 2,3-Diaminonaphthalene, ($C_{10}H_{10}N_2$) or DAN



2.2 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 5 to 5000 µL (model PIPTMAN P, GILSON), were used for preparation of the experimental solutions.

2.3 Preparation of $HClO_4$ solution

$HClO_4$ solution 0.20 M at pH=0.22 was prepared from $HClO_4$ (70%). The concentration of $HClO_4$ was determined using a standard solution of NaOH.

2.4 Preparation of stock solutions (a) and (b) of Se (IV)

Stock solutions of Se (IV) 0.01 M, i.e. 789.6 µg.mL^{-1} (a) and 0.1 mM, i.e. 7.896 µg.mL^{-1} (b) were prepared from H_2SeO_3 using $HClO_4$ solution. The concentration of Se (IV) was determined using reference method [2]. All working solutions for voltammetric investigations were prepared by dilution of the stock solutions of Se (IV) (a or b) with $HClO_4$ solution.

2.5 Preparation of modified gold electrode ($GEM_{DAN}N$)

Gold electrode was first polished, rinsed with deionized water and ultrasonicated successively in a 1:1 aqueous solution of nitric acid and an ethanol solution for 3 min and then dried. A modified solution was prepared by putting 4.5 mL of DAN (0.8 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 0.36 mg.mL^{-1} DAN and 3% v/v nafion). A modified gold electrode was prepared by placing 5μL from modified solution onto the dry electrode with a micro syringe. The electrode was dried to evaporate the solvent and rinsed with deionized water ($GEM_{DAN}N$).

2.6 Preparation of multi-modified gold electrode ($GEM_{DAN-OPDA}N$)

Gold 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 0.25mL of DAN (0.8 mg.mL^{-1}), 4.75 mL of OPDA (10 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 0.02 mg.mL^{-1} DAN, 4.75 mg.mL^{-1} OPDA and 3% v/v nafion). A multi-modified gold 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 ($GEM_{DAN-OPDA}N$).

2.7 Sample preparation

A commercial formulation (as tablet) were used for the analysis of Se (IV) by using DPASVA with $GEM_{DAN}N$ or $GEM_{DAN-OPDA}N$. The pharmaceutical formulations were subjected to the analytical procedures:

(1) **DaVita Silver Plus** tablets, Ultra Medica, Sydnaya–SYRIA, each tablet contains: 70 μg Selenium.

(2) **Daily-Vit** tablets, Biomed, Damascus–SYRIA, each tablet contains: 70 μg Selenium.

(3) **Adult Vit Silver** tablets**,** Aphamea, Hama–SYRIA, each tablet contains: 25 μg Selenium.

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

(5) **Cenvite Silver** tablets, Pharmasyr Co., Damascus–SYRIA, each tablet contains: 20 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. Five stock solutions of pharmaceuticals: **DamVita Silver Plus, Daily-Vit, Adult Vit Silver, Cenvite and Cenvite Silver** which content: 2100, 2100, 750, 750 and 600 ng.mL^{-1} of Se (IV), respectively.

2.8 Working solutions of pharmaceuticals

These solutions were prepared by diluting 1.19, 1.19, 3.33, 3.33 and 4.17mL of stock solutions of pharmaceuticals respectively to 100 mL with $HClO_4$ solution (each one content 25 ng.mL^{-1} selenium).

2.9 Working standard additions solutions of pharmaceuticals

These solutions were prepared as the follows: same mentioned volumes of stock solutions of pharmaceuticals with 0.000, 0.100, 0.200, 0.400 and 0.600 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 7.896, 15.792, 31.584 and 47.376 ng.mL^{-1} selenium from standard additions solutions of Se (IV), respectively.

2.10 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 (-350 mV) was applied to the modified electrode for a certain time. The potential scanned was from +400 to +1250 mV by differential pulse anodic stripping voltammetry using the auto-scan facility. The peak height was measured at 995 to 1010 mV.

3. RESULTS AND DISCUSSION

3.1 Voltammetric behavior

The differential pulse anodic stripping voltammograms using the procedure described above with an electrode modified $GEM_{DAN}N$ or multi-modified $GEM_{DAN-OPDA}N$ show that the sensitivity increased approximately 50 times ($C_{Se(IV)} \geq 1x10^{-9}$ M) by using $GEM_{DAN-OPDA}N$. While the sensitivity by using $GEM_{DAN}N$ or GEMO-PN [6] not reached less than $5x10^{-8}$ M.

3.2 Effect of pH solution

Effect of pH on differential pulse anodic stripping voltammograms of Se (IV) using $GEM_{DAN}N$ or $GEM_{DAN-OPDA}N$ were studied. It was found that the best pH solution 0.22.

3.3 Effect of modified and multi-modified gold electrode composition

The effect of the nafion and DAN concentrations in modified solution for formation $GEM_{DAN}N$ on the peak current was studied. The peak current reached its maximum when the concentrations of nafion and DAN were 3%v/v and 0.36 $mg.mL^{-1}$, respectively.

The effect of the nafion, DAN and OPDA concentrations in multi - modified solution for formation $GEM_{DAN-OPDA}N$ on the peak current was studied. The peak current reached its maximum when the concentrations of nafion, DAN and OPDA were 3%v/v, 0.02 $mg.mL^{-1}$ and 4.75 $mg.mL^{-1}$, respectively.

3.4 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 -0.350 V on $GEM_{DAN}N$ and $GEM_{DAN-OPDA}N$.

3.5 Effect of accumulation time

The peak current increases with increasing accumulation time. The current is nearly linear from 50 to 400 s. The best time was 300 s for Se (IV) concentrations $5x10^{-8}$ -$1x10^{-6}$ M on $GEM_{DAN}N$ and 300 s for Se (IV) concentrations $1x10^{-9}$ -$1x10^{-6}$ M on $GEM_{DAN-OPDA}N$.

3.6 Effect of other factors

The other influencing factors on the peak current were studied, it found that the preferred values are as follows: waiting time, drop modified size, initial potential, final potential, peak potential, scan rate, stirring speed and temperature of solution were 5s, 5µL, +400 mV, +1250 mV, 995-1010 mV, 10 mV, 1000 rpm and 25°± 0.5°C, respectively.

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) are affecting the Se (IV) determination were examined. The optimum parameters for DPASV determination of selenium (IV) were selected and presented in the (Table 1).

4. 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 $GEM_{DAN}N$

and $GEM_{DAN-OPDA}N$ by DPASVA showed linear proportionality over the concentration range from 3.948 to 78.96 $ng.mL^{-1}$ (5×10^{-8} to $1x10^{-6}$ M) of Se (IV) on $GEM_{DAN}N$ and from 0.07896 to 78.96 $ng.mL^{-1}$ (1×10^{-9} to $1x10^{-6}$ M) of

Se (IV) on $GEM_{DAN-OPDA}N$ with accumulation (deposition) time 300 s (Figures 1-3). Regression equations and correlation coefficient were as the follows:

$y = 0.2552x + 0.0858$ (R^2=0.9997) for the concentration of Se (IV) from 3.948 to 78.96 $ng.mL^{-1}$ (5×10^{-8} to $1x10^{-6}$ M) and $y = 0.5279x + 0.1836$ (R^2=0.9997) for the concentration of Se (IV) from 0.07896 to 78.96 $ng.mL^{-1}$ (1×10^{-9} to $1x10^{-6}$ M) at $GEM_{DAN}N$ and at $GEM_{DAN-OPDA}N$, respectively, In this method it was determined a low concentration of Se (IV) 3.948 $ng.mL^{-1}$ (5×10^{-8} M) with relative standard deviation did not exceed ±4.2% at $GEM_{DAN}N$ and a very low concentration 0.07896 $ng.mL^{-1}$ (1×10^{-9} M) of Se (IV) with relative standard deviation did not exceed ±4.9% at $GEM_{DAN-OPDA}N$ (Tables 2 and 3). This method showed very sensitive results for the determination of Se (IV) on $GEM_{DAN-OPDA}N$ more than the results obtained by using $GEM_{DAN}N$ or $GEM_{OPDA}N$ about 50 times. The results are in good agreement with those obtained by the reference method [8].

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

Parameters	**Operating modes**		
	o-PDA (GEM-O-PN) [6])	**DAN ($GEM_{DAN}N$)**	**Mixture of DAN and O-PDA ($GEM_{DAN-OPDA}N$)**
Accumulation (deposition) time	300 s		
Accumulation potential	-350 mV		
Supporting electrolyte	0.20 M $HClO_4$		
Indicator electrode	Rotating disk gold electrode (RDGE)		
pH solution	0.22		
Modified electrode composition	4.75 $mg.mL^{-1}$ O-PDA + 3% v/v nafion-ethanol	0.36 $mg.mL^{-1}$ DAN + 3% v/v nafion-ethanol	0.02 $mg.mL^{-1}$ of DAN +4.75 mg/ml of O-PDA + 3% v/v nafion-ethanol
Waiting time	5 s		
Drop modified size	5µL		
Initial potential	+400 mV		
Final potential	+1250 mV		
Peak potential	995-1010 mV		
Scan rate	10 mV/s		
Stirring speed	1000 rpm		
Temperature of solution	25°± 0.5°C		

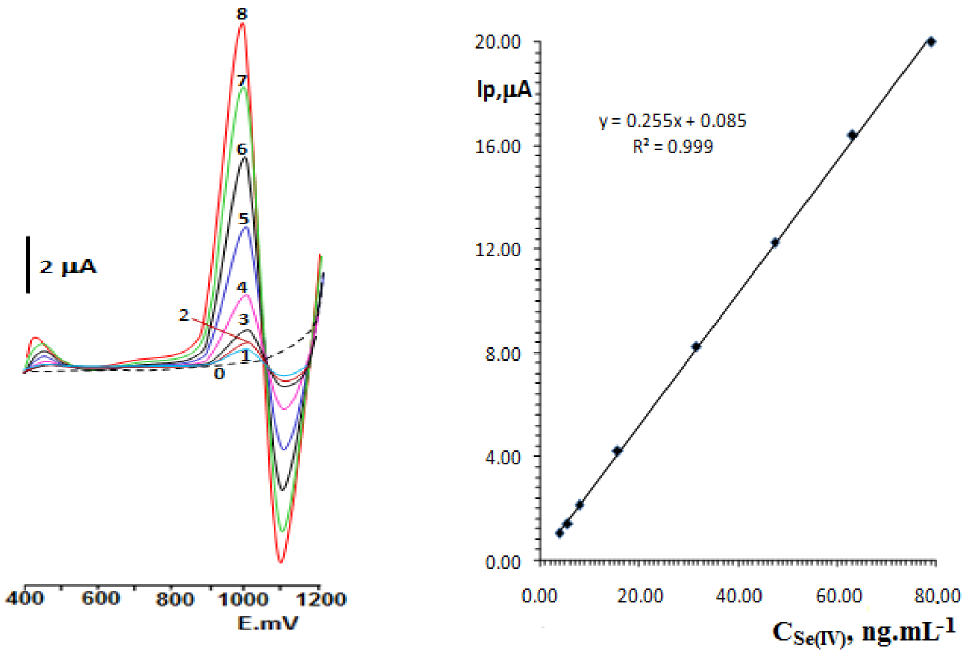


Fig.1. Determination of Se (IV) in presence of 0.20 M $HClO_4$ by DPASVA using $GEM_{DAN}N$. when $C_{Se(IV)}$:
0- electrolyte, 1- 3.948, 2- 5.5272, 3- 7.896, 4- 15.792, 5- 31.584, 6- 47.376, 7- 63.168 and 8- 78.96 ng.mL^{-1}.
(accumulation time 300s, accumulation potential -350 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C, n=5).

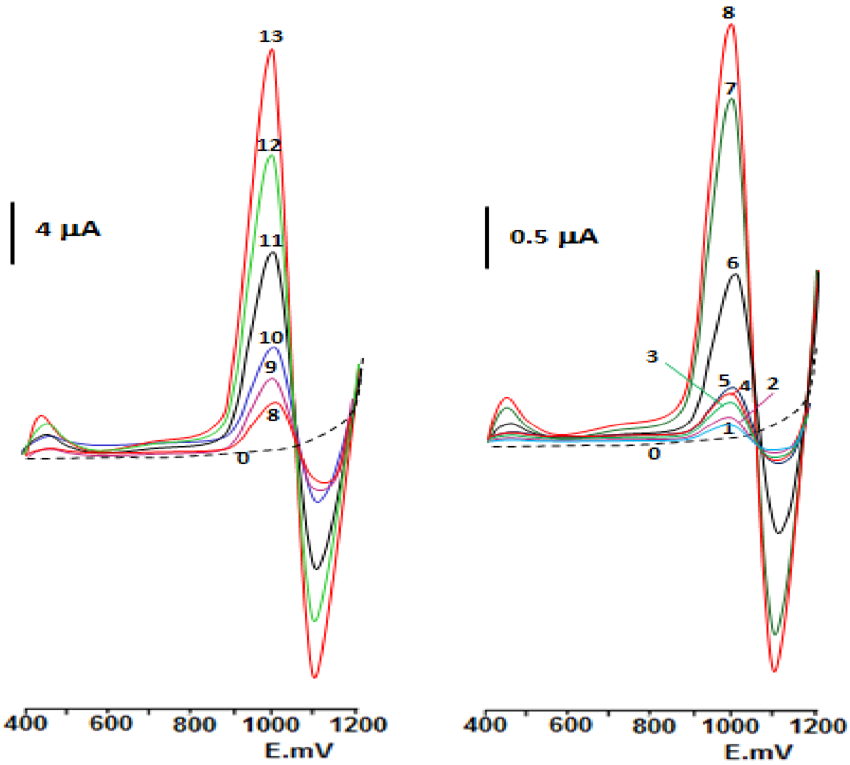


Fig.2. Determination of Se (IV) in presence of 0.20 M $HClO_4$ by DPASVA using $GEM_{DAN-OPDA}N$ when $C_{Se($
0- electrolyte, 1- 0.07896, 2- 0.15792, 3- 0.47376, 4- 0.63168, 5- 0.7829, 6- 3.948, 7- 7.896, 8- 9.87, 14.805, 10- 19.74, 11- 39.48, 12- 59.22 and 13- 78. 96ng.mL^{-1}. (accumulation time 300s, accumulation potential -350 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C, n=5).

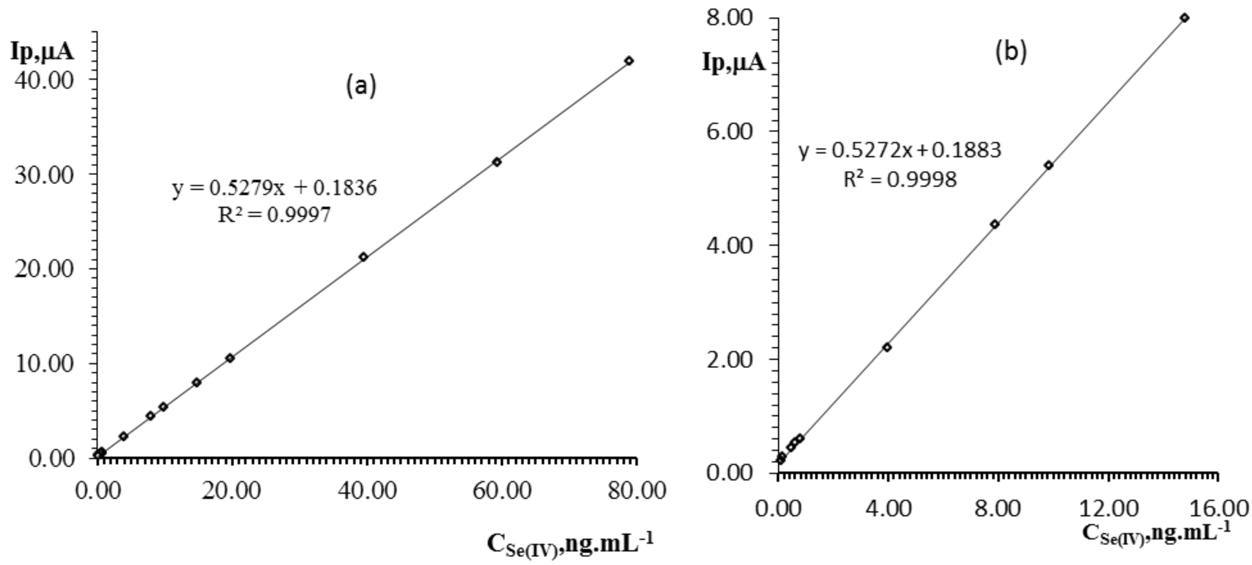


Fig.3. Calibration curves for the determination of Se (IV) using DPASVA on $GEM_{DAN-OPDA}N$ in the optimum conditions. $Ip=f(C_{Se(IV)})$ (a) 0.07896- 78.96 $ng.mL^{-1}$, (b) 0.07896- 14.805 $ng.mL^{-1}$.

Table 2: Determination of selenium (IV) by DPASVA on $GEM_{DAN}N$ for $C_{Se(IV)}$ 3.948 - 78.960 $ng.mL^{-1}$; Where (a) using O-PDA [6] and (b) using DAN (accumulation time: 300 s, accumulation potential -350 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)	gold electrode modified	$\bar{x}$, $ng.mL^{-1}$ (found)	SD, $ng.mL^{-1}$	$\frac{SD}{\sqrt{n}}$, $ng.mL^{-1}$	$\bar{x} \pm \frac{t.SD}{\sqrt{n}}$, $ng.mL^{-1}$	RSD %
3.948	(a)	3.820	0.145	0.0650	3.820± 0.180	3.8
	(b)	3.582	0.150	0.0673	3.582± 0.187	4.2
5.5272	(a)	5.495	0.198	0.0885	5.495± 0.246	3.6
	(b)	5.150	0.206	0.0921	5.150± 0.256	4.0
7.896	(a)	8.112	0.284	0.127	8.112± 0.352	3.5
	(b)	7.893	0.284	0.127	7.893± 0.352	3.6
15.792	(a)	16.225	0.487	0.218	16.225± 0.604	3.0
	(b)	16.121	0.532	0.238	16.121± 0.660	3.3
31.584	(a)	31.222	0.937	0.420	31.222± 1.163	3.0
	(b)	31.850	0.987	0.441	31.850± 1.226	3.1
47.376	(a)	48.092	1.298	0.580	48.092± 1.611	2.7
	(b)	47.689	1.431	0.640	47.689± 1.776	3.0
63.168	(a)	62.728	1.568	0.701	62.728± 1.947	2.5
	(b)	63.927	1.598	0.715	63.927± 1.984	2.5
78.960	(a)	78.951	1.737	0.777	78.951± 2.156	2.2
	(b)	78.034	1.795	0.803	78.034± 2.229	2.3

Table 3: Determination of selenium (IV) by DPASVA on $GEM_{DAN-OPDA}N$ for $C_{Se(IV)}$ 0.07896 - 0.7896 $ng.mL^{-1}$ (accumulation time 300 s, accumulation potential -350 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)	$\bar{x}$, $ng.mL^{-1}$ (found)	SD, $ng.mL^{-1}$	$\frac{SD}{\sqrt{n}}$, $ng.mL^{-1}$	$\bar{x} \pm \frac{t.SD}{\sqrt{n}}$, $ng.mL^{-1}$	RSD %	found [8]	
						$\bar{x}$ ±SD, $ng.mL^{-1}$	RSD %
0.07896	0.0722	0.00354	0.001582	0.0722±0.0044	4.9	0.0772±0.0062	4.8
0.15792	0.1549	0.00744	0.00333	0.1549±0.0033	4.8	0.1552±0.0073	4.7
0.47376	0.4869	0.02191	0.00980	0.6426±0.0272	4.5	0.4902±0.023	4.6
0.63168	0.6426	0.0283	0.0126	0.7999±0.035	4.4	0.6486±0.029	4.5
0.78290	0.7999	0.0320	0.0143	0.7999±0.040	4.0	0.7705±0.034	4.4
3.948	3.816	0.1450	0.0649	3.816±0.180	3.8	3.902±0.153	3.9
7.896	7.913	0.2849	0.1274	7.913±0.354	3.6	7.836±0.290	3.7
9.870	9.886	0.3446	0.1547	9.886±0.430	3.5	9.845±0.364	3.7
14.805	14.817	0.5038	0.2253	14.817±0.625	3.4	14.860±0.550	3.7
19.740	19.542	0.6449	0.2884	19.542±0.800	3.3	19.660±0.727	3.7
39.480	39.933	1.3178	0.5894	39.933±1.636	3.3	40.718±1.470	3.6
59.220	58.754	1.9389	0.8671	58.754±2.407	3.3	58.984±2.064	3.5
78.960	79.122	2.5319	1.1323	79.122±3.143	3.2	78.478±2.750	3.5

5. APPLICATIONS

Many applications for the determination of Se (IV) in some pharmaceutical preparations by DPASVA on $GEMDAN_{-OPDA}N$ using the optimum parameters were proposed. Standard addition curves for determination of Se (IV) in different pharmaceutical preparations (DamVita Silver Plus, Daily-Vit, Adult Vit Silver, Cenvite and Cenvite Silver) were used. Regression equations and correlation coefficients were included in (Table 4). Standard additions on 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 2.8, 2.8, 1.0, 1.0 and 0.8 for all pharmaceuticals content 70, 70, 25, 25 and 20 µg/tab, respectively. The results of quantitative analysis for Se (IV) in the pharmaceutical preparations using this method included in (Table 5). 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: Regression equations and correlation coefficients for determination of $C_{Se(IV)}$ in pharmaceutical preparations using DPASV on $GEM_{DAN-OPDA}N$ (accumulation time 300 s, accumulation potential -350 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.**
DamVita Silver Plus tablets, Ultra Medica, Sydnaya–SYRIA	70	y = 0.5278x + 13.459	R^2=0.9988	25.50	m = 2.8 m'=71.40
Daily-Vit tablets, Biomed, Damascus–SYRIA	70	y = 0.5275x + 13.599	R^2=0.9990	25.78	m = 2.8 m'=72.18
Adult Vit Silver tablets, Aphamea, Hama–SYRIA	25	y = 0.5276x + 13.063	R^2=0.9998	24.76	m = 1.0 m'= 24.76
Cenvite tablets, Pharmasyr Co., Damascus – SYRIA	25	y = 0.5270x + 13.175	R^2=0.9996	25.00	m =1.0m'=25.00
Cenvite Silver tablets, Pharmasyr Co., Damascus–SYRIA	20	y = 0.5273x + 13.472	R^2=0.9993	25.55	m =0.8m'=20.44

*y= a.x+b=0, x= $C_{Se(IV)}$ ($ng.mL^{-1}$) = m' = intercept(b)/slope(a).

Table 5: Determination of Se (IV) in pharmaceutical preparations using DPASV on $GEM_{DAN-OPDA}N$ (accumulation time 300 s, accumulation potential -350 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%**	**Assay %**
DamVita Silver Plus tablets, Ultra Medica, Sydnaya–SYRIA	70	71.40	2.8	102.00
Daily-Vit tablets, Biomed, Damascus–SYRIA	70	72.18	2.6	103.11
Adult Vit Silver tablets, Aphamea, Hama–SYRIA	25	24.76	3.2	99.04
Cenvite tablets, Pharmasyr Co., Damascus – SYRIA	25	25.00	3.0	100.00
Cenvite Silver tablets, Pharmasyr Co., Damascus–SYRIA	20	20.44	3.4	102.20

6. 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) [17].

6.1 Selectivity

Selectivity test determines the effect of excipients on the assay result. To determine the selectivity of the method, 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 no interference.

6.2 Linearity

In the proposed methods, linear plots (n= 5) with good correlation coefficients were obtained in the concentration ranges of y = 0.2552x + 0.0858 (R^2=0.9997) on $GEM_{DAN}N$ for the concentration from 3.948 to 78.96 $ng.mL^{-1}$ and y = 0.5279x + 0.1836 (R^2=0.9997) for the concentration from 0.07896 to 78.96 $ng.mL^{-1}$, respectively, on $GEMDAN_{-OPDA}N$. In this method a very low concentration 0.07896 $ng.mL^{-1}$ (1×10^{-9} M) of Se (IV) on $GEM_{DAN-OPDA}N$ was determined.

6.3 Precision and Accuracy

The precision and accuracy of proposed method was 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 14.805 $ng.mL^{-1}$. The proposed method was validated statistically and through recovery studies. It was successfully applied for the determination of Se (IV) in pure and dosage forms with percent recoveries ranged from 99.3% to 100.8% (Table 6).

Table 6: Results of recovery studies (n=5).

Level	% Recovery
80%	99.3
100%	100.5
120%	100.8

6.4 Repeatability

The repeatability was evaluated by performing 10 repeat measurements for 3.948 $ng.mL^{-1}$ 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 3.936± 0.143 $ng.mL^{-1}$ and the percentage recovery was found to be 99.70 ± 3.6 with RSD of 0.036. These values indicate that the proposed method has high repeatability for Se (IV) analysis.

6.5 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 0.014 and 0.042 $ng.mL^{-1}$, respectively.

6.6 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 (-350±5 mV) and C_{HClO4} (0.20±0.01 M), (Table 7) indicates the robustness of the proposed method. I_p was measured and assay was calculated for five times.

Table 7: Robustness of the proposed DPASVA method.

Experimental parameter variation	Average recovery (%) *
	$C_{Se(IV)}$ =14.805 ng.mL^{-1}
Temperature	
15°C	99.7
25°C	100.1
pH	
0.21	100.5
0.23	99.9
Accumulation potential	
-345 mV	100.0
-355 mV	100.4
C_{HClO4}	
0.19 mol/L	99.8
0.21 mol/L	100.3

* n=5.

6.7 Specificity

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

6.8 THE HOMOGENIZATION OF TABLETS

The homogenization of tablets in terms of the weight and the amount of drug was studied. We found that the mean weight and amount drug in the tablets were 1.512 ± 0.012 g (i.e. ±0.797%), 1.516 ± 0.016 g (i.e. ±1.055%), 1.410 ± 0.010 g (i.e. ±0.710%), 1.522 ± 0.022 g (i.e. ±1.445%) and 1.4082 ± 0.008 g (i.e. ±0.568%) for DamVita Silver Plus, Daily-Vit s, Adult Vit Silver, Cenvite and Cenvite Silver tablets, respectively. While the mean amount drug in the tablets was 71.40± 2.00 µg (i.e. ±2.8%), 72.18± 1.88 µg (i.e. ±2.6%), 24.76 ± 0.79 µg (i.e. ±3.2%), 25.00± 0.75 µg (i.e. ±3.0%) and 20.44 ± 0.69 µg (i.e. ±3.4%) for DamVita Silver Plus, Daily-Vit, Adult Vit Silver, Cenvite and Cenvite Silver tablets, respectively; which shows that homogeneity of tablets is good.

7. CONCLUSION

DPASVA of selenium (IV) using $GEM_{DAN}N$ and $GEM_{DAN-OPDA}N$ with an aqueous 0.2 M $HClO_4$ medium of pH 0.22 according to the optimal conditions were applied. Liner calibration graphs, $I_p=f(C_{Se(IV)})$, were obtained in the concentration ranges of 3.948 -78.96 $ng.mL^{-1}$ with relative standard deviations (RSD) ≤ 4.2%, the detection limit was 0.056 $ng.mL^{-1}$ on $GEM_{DAN}N$ and the concentration ranges of 0.07896 -78.96 $ng.mL^{-1}$ with relative standard deviations (RSD) ≤ 4.9%, the detection limit was 0.014 $ng.mL^{-1}$ on $GEM_{DAN-OPDA}N$. This method showed a good accumulation efficiency for selenium and a good resistance to interferences from metal ions as well as those associated with selenium in pharmaceuticals. This method showed very sensitive results for the determination of Se (IV) than that obtained using $GEM_{DAN}N$ or GEM-o-PN. The results for the determination of Se(IV) using $GEM_{DAN-OPDA}N$ were more sensitive and accurate than the results obtained by using $GEM_{DAN}N$; the sensitivity was increased about 50 times.

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