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Development of Gold Electrode Modified With Sodium Diethyldithiocarbamate-Nafion to Determine Selenium (IV) in Bulk and in Dosage Formulations Using Differential Pulse Anodic Stripping Voltammetric Analysis

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Abstract

The effect of gold electrode modified with sodium diethyldithiocarbamate-Nafion ($GEM_{DDTC}N$) on determination of selenium (IV) using differential pulse anodic stripping voltammetric analysis (DPASVA) was 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 $HClO_4$ (0.1 M) and HCl (0.002 M) medium of pH 0.22 at an accumulation potential of -350 mV (vs. Ag/AgCl) and an accumulation time of 200 s. Under the optimum conditions, liner calibration graph, $I_p=f(C_{Se}{}^{4+})$ was obtained in the concentration ranges of $2.5x10^{-8}$ M (1.974 ng/mL) to $1x10^{-6}$ M (78.96 ng/mL) with relative standard deviations (RSD) $\leq$ 4.0%. 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 ($GEM_{DDTC}N$) was more sensitive and accurate than that obtained using bare gold, $GEM_{DAN}N$ and $GEM_{OPDA}N$ electrodes (the sensitivity was increased about 4000 times and about 2 times, respectively).

Keywords: Sodium Diethyldithiocarbamate, Nafion, Selenium, Differential pulse anodic stripping voltammetry

Introduction

A new sensitive and selective pulse polarographic method for the determination of Se(IV) next to interfering ions is described. This method is based on the highly sensitive peak formed by the reaction of Se(IV) with o-phenylenediamine in Britton-Robinson buffer solution (pH 2.5) at 0.08 V (vs. Ag/AgCl). A linear calibration graph is obtained for Se(IV) at a concentration of 5.0 x 10^{-8} to 6.8 x 10^{-5} M [1].

The adsorptive voltammetric behavior of Se(IV) on the hanging mercury drop electrode (HMDE) in the presence of o-phenylenediamine (o-PDA) has been investigated. Experimental results show that the Se(IV) complex with o-PDA can be adsorbed on the surface of the HMDE, yielding two peaks at -0.13 V and -0.62 V (vs. Ag/AgCl). The detection limit of the adsorption voltammetry, established from the second peak at -0.62 V, is as low as 4×10^{-10} mol/L [2].

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) [3].

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 [4].

The o-phenylenediamine in situ modified electrode, which was used to detect the trace selenium in the human body was studied. The detection limit is 3.2× 10^{-9} mol/L and the average percentage of recovery is 97.0 ± 4.3% [5].

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 for 10 min preconcentration [6].

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 saturated 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 μg/L with 5 min accumulation [7].

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} mol/L with relative standard deviations (RSD) 4.5 % [8].

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 ≤ 4.6% [9].

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} ($GEMD_{ab}V_EN$) has been studied Liner calibration graph was obtained in the concentration ranges of 1×10^{-9} - 1×10^{-6} mol/L with relative standard deviations (RSD) 4.8 % [10].

Differential pulse anodic stripping voltammetric analysis (DPASVA) of selenium(IV) using a gold electrode modified with o-Phenylenediamine-nafion (GEMO-PN) 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 with relative standard deviations (RSD)≤3.8%, and the detection limit was 0.048 ng/mL [11].

The effect of gold electrode modified with 2,3-Diaminonaphthalene ($GEM_{DAN}N$) and gold electrode multi-modified with a mixture o-phenylenediamine and 2,3-diaminonaphthalene-nafion ($GEM_{DAN\text{-}OPDA}N$) on determination of selenium (IV) using differential pulse anodic stripping voltammetric analysis (DPASVA) has been studied. Selenium (IV) was determined. liner calibration graph, were obtained in the concentration ranges of $5x10^{-8}$ - $1x10^{-6}$ M (3.948 - 78.96 ng/mL) with relative standard deviations (RSD)≤4.2%, the detection limit was 0.056 ng/mL on $GEM_{DAN}N$ and the concentration ranges of $1x10^{-9}$ -$1x10^{-6}$ M (0.07896 -78.96 ng/mL) with relative standard deviations (RSD)≤5.0%, the detection limit was 0.0012 ng/mL on $GEM_{DAN\text{-}OPDA}N$ [12].

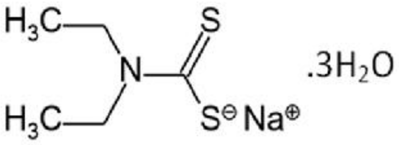
Spectrophotometric determination of selenium (IV) with 2-Mercaptobenzothiazol was also suited [13]. Dispersive liquid–liquid microextraction using diethyldithiocarbamate as a chelating agent and the dried-spot technique for the determination of Fe, Co, Ni, Cu, Zn, Se and Pb by energy-dispersive X-ray fluorescence spectrometry [14].

In the present work, the effect of gold electrode modified with sodium diethyldithiocarbamate-Nafion ($GEM_{DDTC}N$) using differential pulse anodic stripping voltammetric analysis (DPASVA) has been studied.

Experimental

Reagents

Nafion perfluorinated ion-exchange resin in ethanol (3% v/v) was purchased from Aldrich. Sodium diethyldithiocarbamate.tryhidrate, $NaS_2CN(C_2H_5)_2.3H_2O$, mol. mass 225.3 g (Scheme1) was from SIGMA. H_2SeO_3 and all other reagents were of analytical grade from Merck [15]. An $HClO_4$ solution 0.10 M and HCl 0.002 M were used at pH=0.22. A stock solution (a) of Se(IV): 789.6 µg/mL (0.01 mol/L) and a stock solution (b) of Se(IV):7.896 µg/mL (0.1 mmol/L) 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.



Scheme 1: Sodium diethyldithiocarbamate, $(NaS_2CN(C_2H_5)_2.\ 3H_2O)$

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 20 to 5000 μL (model PIPTMAN P, GILSON), and a micro syringe which size 10μL were used for preparation of the experimental solutions.

Preparation of modified gold electrode ($GEM_{DDTC}N$).

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 1mL of DDTC (2.5 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 0.25 mg/mL DDTC and 3% v/v Nafion). A modified gold electrode was prepared by placing 10μL from 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 ($GEM_{DDTC}N$).The pharmaceutical formulations were subjected to the analytical procedures:

(1) ***DamVita 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**,** Afhamea, 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 of Se(IV), respectively were studied.

Working solutions of pharmaceuticals

These solutions were prepared by diluting 1.19, 1.19, 3.33, 3.33 and 4.17 mL of stock solutions of pharmaceuticals respectively to 100 mL with $HClO_4$ solution (each one content 25 ng/mL 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, 0.100, 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 selenium (from pharmaceutical formulations) with 7.896, 15.792, 31.584 and 47.376 ng/mL 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 (-350 mV) was applied to the modified electrode for a certain time. The potential scanned was from +0.00 to +1250 mV by differential pulse anodic stripping voltammetry using the auto-scan facility. The peak height was measured at 990-1010 mV.

Results and Discussion

Voltammetric behavior

The differential pulse anodic stripping voltammograms using the procedure described above with a bare Au electrode ($C_{Se(IV)}$ ≥$1x10^{-4}$ mol/L, RSD=6.8%), while an electrode modified with ($GEM_{DDTC}N$) shows that the peak potential shifted slightly from 990 mV to 1010 mV and the sensitivity increased ($C_{Se(IV)}$ ≥$2.5x10^{-8}$ mol/L) when the ($GEM_{DDTC}N$) was introduced to modify the coating.

Effect of modified electrode composition

The effect of the Nafion and sodium diethyldithiocarbamate, tryhidrate, concentrations in modified solution for formation gold electrode modified with sodium diethyldithiocarbamate .tryhidrate-Nafion ($GEM_{DDTC}N$) on the peak current were studied. The peak current reached its maximum when the concentration Nafion is 3% v/v and DDTC is 2.5 mg/mL.

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, see (Figures 1 & 2).

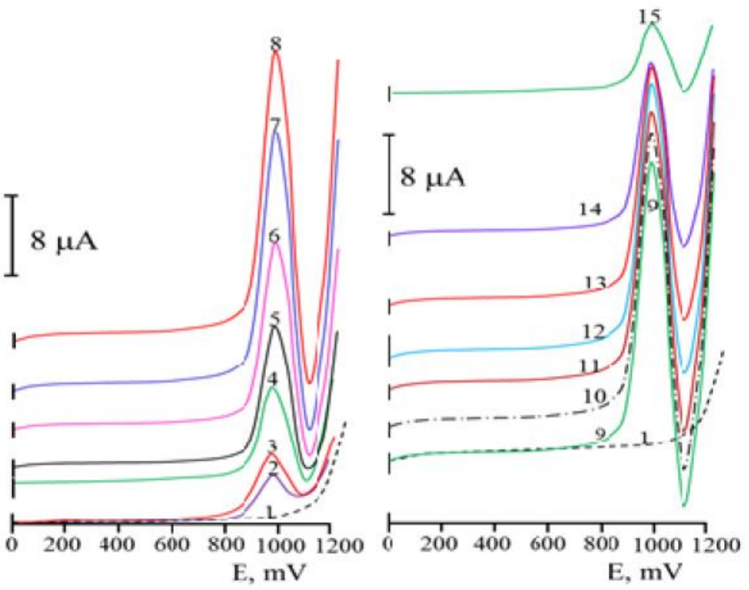


Fig.1. Effect of accumulation potential on differential pulse anodic stripping voltammograms of Se(IV) 78.96 ng/mL using DDTC–Nafion modified gold electrode, pH=0.22, scan rate 10 mV/s and temperature 25°± 0.5°C at of accumulation potential: 1) Electrolyte (0.1M $HClO_4$ + 0.002M HCl), 2) -50 mV, 3) –100mV, 4) -150mV , 5) -200mV , 6) -250mV , 7) -300mV , 8) -325mV , 9)-350mV ,10) -375mV, 11) -400mV , 12) -425mV , 13) -450 mV , 14) -500mV, 15) -600 mV.

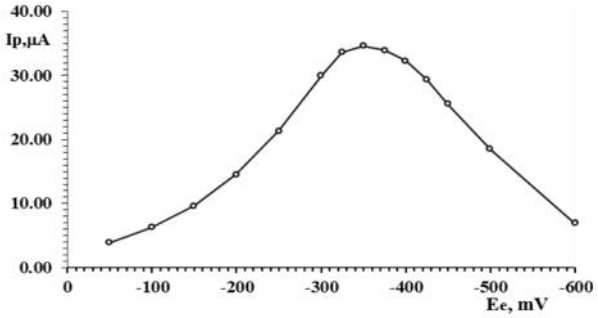


Fig.2. Effect of accumulation potential on differential pulse anodic stripping voltammograms of Se(IV) 78.96 ng/mL using DDTC–Nafion modified gold electrode, pH=0.22, scan rate 10 mV/s and temperature 25°± 0.5°C).

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 400 s. Various parameters (electrolyte, 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, see (Figure 3). The optimum parameters for DPASV determination of selenium (IV) were selected and presented in the (Table 1).

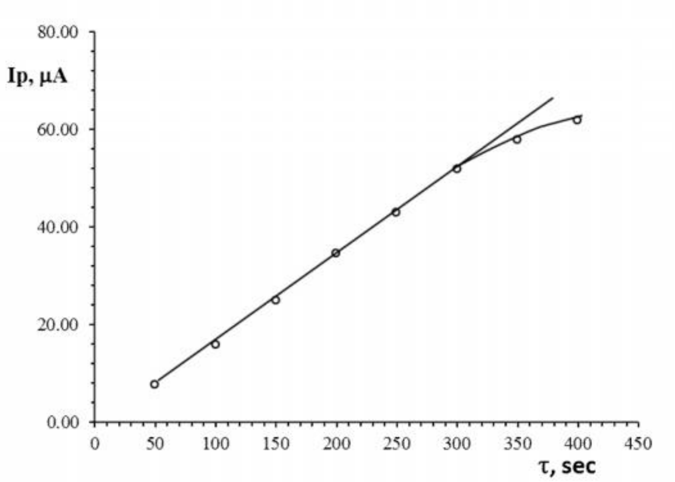


Fig.3. Effect of accumulation time on differential pulse anodic stripping voltammograms of Se(IV) 78.96 ng/mL using DDTC–Nafion modified gold electrode (accumulation potential -350 mv, pH=0.22, scan rate 10 mV/s and temperature 25°± 0.5°C).

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	-350 mV
Supporting electrolyte	0.10 M $HClO_4$ & 0.002 M HCl
Indicator electrode	Rotating disk gold electrode (RDGE)
pH solution	0.22
Modified electrode composition	0.25mg/mL DDTC and 3% v/v Nafion-Ethanol
Waiting time	5 s
Drop modified size	10µL
Initial potential	+000 mV
Final potential	+1200 mV
Peak potential	990-1010 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 0.10 M $HClO_4$ and 0.002M HCL on ($GEM_{DDTC}N$) by (DPASVA) showed linear proportionality over the concentration range from 1.974 to 78.96 ng/mL (2.5×10^{-8} to $1x10^{-6}$ mol/L) of Se(IV) with accumulation (deposition) time 200 s., see (Figure 4). Regression equations and correlation coefficient were as the follows: $y = 0.4375x + 0.0006$ ($R^2=0.9997$) in this method a very low concentration 1.974 ng/mL (2.5×10^{-8} mol/L) with relative standard deviation not exceed ±4.0% (Table 2). This method showed a very sensitive results for the determination of Se(IV) on ($GEM_{DDTC}N$) more than that obtained using bare gold, $GEM_{DAN}N$ and $GEM_{OPDA}N$ electrodes (the sensitivity was increased about 4000 times and about 2 times, respectively).

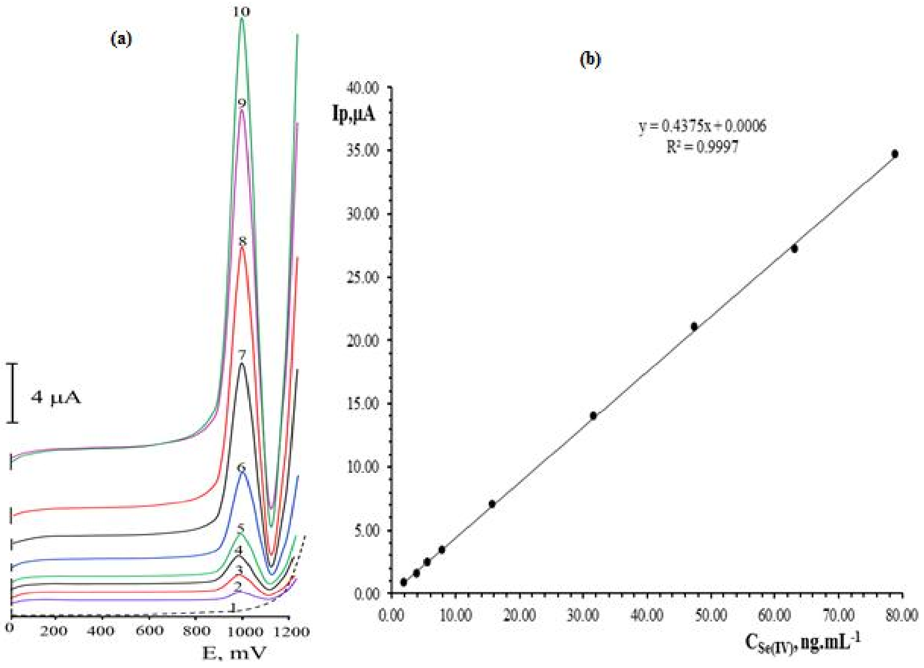


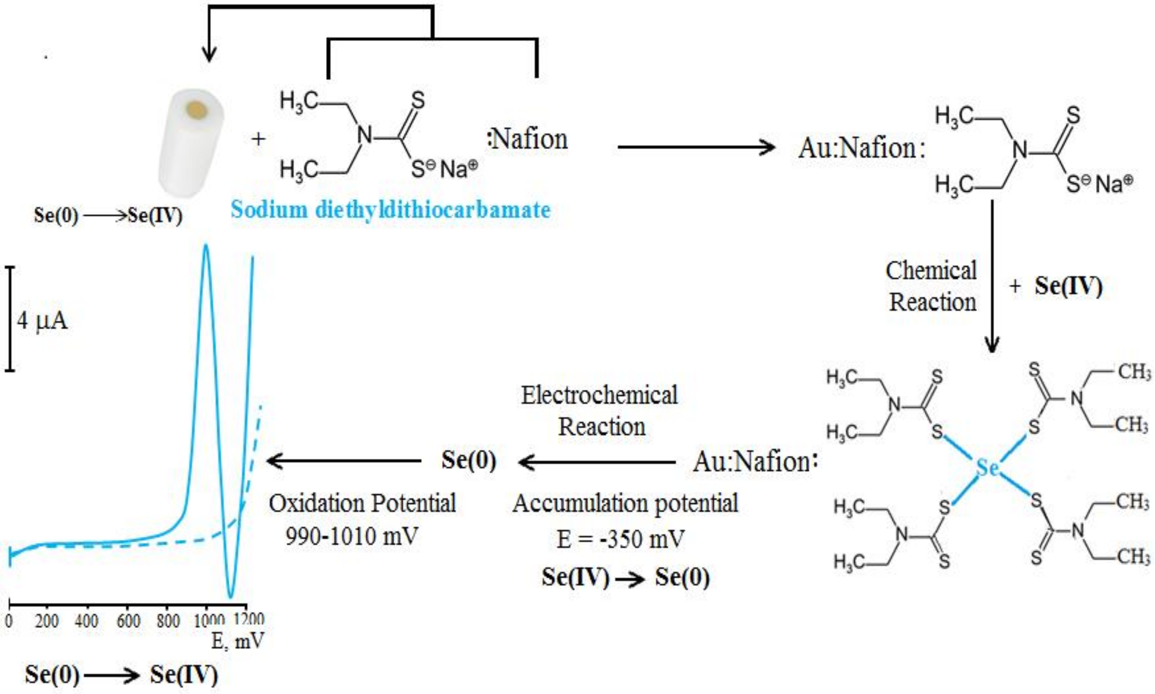
Fig.4. (a) Differential pulse anodic stripping voltammograms of Se(IV) on DDTC-Nafion modified gold electrode at pH=0.22 when $C_{Se(IV)}$: 1- electrolyte, 2-1.974, 3- 3.948, 4- 5.5272, 5- 7.896, 6- 15.792, 7- 31.584, 8- 47.376, 9-63.168, and 10- 78.96 ng/mL . (b) $I_p = f(C_{Se(IV)})$ for the determination of Se(IV) in presence of 0.10 M $HClO_4$ and 0.002 M HCl by DPASVA using a DDTC-Nafion modified gold electrode (accumulation time 200 s, accumulation potential -350 mV, pH=0.22, scan rate 10 mV/s and temperature 25°± 0.5°C).

Table 2: Determination of selenium(IV) by DPASVA on a DDTC–Nafion modified gold electrode (accumulation time 200 s, accumulation potential -350 mV, pH=0.22, scan rate 10 mV/s, temperature 25°± 0.5°C and n=5, t=2.776).

x_i, ng/mL (taken)	$\bar{x}$, ng/mL (found)	SD, ng/mL	, ng/mL $\frac{SD}{\sqrt{n}}$	$\bar{x} \pm \frac{t.SD}{\sqrt{n}}$, ng/mL	RSD %
1.974	1.959	0.078	0.035	1.959±0.097	4.0
3.948	3.765	0.139	0.062	3.765±0.173	3.7
5.527	5.525	0.188	0.084	5.525±0.233	3.4
7.896	7.778	0.257	0.115	7.778±0.319	3.3
15.792	15.999	0.480	0.215	15.999±0.596	3.0
31.584	31.907	0.925	0.414	31.907±1.149	2.9
47.376	47.999	1.248	0.558	47.999±1.549	2.6
63.168	62.170	1.492	0.667	62.170±1.852	2.4
78.960	79.244	1.585	0.709	79.244±1.968	2.0

The proposed mechanism of Se(IV) on ($GEM_{DDTC}N$)

The disk of gold electrode modified was developed by sodium diethyldithiocarbamate. This reagent attracts selenium and is associated with it on the surface of the electrode, forming a complex ratio of 4:1; [($DDTC)_4$: Se]. On the surface of the electrode by applying accumulation potential -350 mV, after which the oxidation of the metallic selenium to the quaternary selenium as the following mechanism.



Scheme 2: Electrochemical mechanisms of selenium on modified gold electrode($GEM_{DDTC}N$).

Applications

Many applications for the determination of Se(IV) in some pharmaceutical preparations by DPASVA on a ($GEM_{DDTC}N$) using the optimum conditions 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 3). 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) 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 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 3: Regression equations and correlation coefficients for determination of $C_{Se(IV)}$ in pharmaceutical preparations using DPASV on ($GEM_{DDTC}N$) (accumulation time 200 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**	**Amount of Se^{4+} (m), µg/tab.**
DamVita Silver Plus tablets, Ultra Medica, Sydnaya–SYRIA	70	y = 0.4377x + 11.226	R^2=0.9998	25.65	m = 2.8 m'=71.81
Daily-Vittablets, Biomed, Damascus–SYRIA	70	y = 0.4373x + 11.259	R^2=0.9992	25.75	m = 2.8 m'=72.09
Adult Vit Silvertablets**,** Afhamea, Hama–SYRIA	25	y = 0.4378x + 10.852	R^2=0.9997	24.79	m = 1.0 m'= 24.79
Cenvitetablets, Pharmasyr Co., Damascus – SYRIA	25	y = 0.4370x + 11.112	R^2=0.9995	25.43	m =1.0m'=25.43
Cenvite Silver tablets, Pharmasyr Co., Damascus–SYRIA	20	y = 0.4376x + 11.353	R^2=0.9991	25.94	m =0.8m'=20.76

*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 ($GEM_{DDTC}N$) (accumulation time 200 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	71.81	2.6	102.59
Daily-Vit tablets, Biomed, Damascus–SYRIA	70	72.09	2.4	102.99
Adult Vit Silver tablets**,** Afhamea, Hama–SYRIA	25	24.79	2.9	99.16
Cenvite tablets, Pharmasyr Co., Damascus – SYRIA	25	25.43	3.0	101.72
Cenvite Silver tablets, Pharmasyr Co., Damascus–SYRIA	20	20.76	3.2	103.80

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) [16].

Selectivity

Selectivity test determines the effect of excipients on the assay result. The results of the tests proved that the effect of the presence of common excipients are no interference.

Linearity

In the proposed methods, linear plots (n= 5) with good correlation coefficients were obtained in the concentration ranges of $y = 0.4375x + 0.0006$ (R^2=0.9997) on a ($GEM_{DDTC}N$) for the concentration from 1.974 to 78.96 ng/mL. In this method a very low concentration 1.974 ng/mL (2.5×10^{-8} mol/L) of Se(IV).

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 15.792 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 99.8% to 101.5% (Table 5).

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

Level	% Recovery
80%	99.8
100%	100.6
120%	101.5

Repeatability

The repeatability was evaluated by performing 10 repeat measurements for 5.527 ng/ml of Se(IV) using the studied method under the optimum conditions in two concentration ranges. The found amount of Se (IV) ($\bar{x} \pm$ SD) was 5.526±0.172 ng/ml and the percentage recovery was found to be 99.98±3.1 with RSD of 0.031. These values indicate that the proposed method has high repeatability for Se (IV) analysis.

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 0.028 and 0.084 ng/mL, 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 (-350±5 mV) and C_{HClO4} (0.10±0.01 mol/L) and C_{HCl}(0.002±0.0001 mol/L). Table 6 was indicates the robustness of the proposed method (I_p was measured and assay was calculated for five times).

Table 6: Robustness of the proposed DPASVA method**.**

Experimental parameter variation	Average recovery (%)* $C_{Se(IV)}$ =15.792ng/mL
Temperature	
20°C	99.9
30°C	101.0
pH	
0.21	100.0
0.23	99.8
Accumulation potential	
-345 mV	100.7
-355 mV	100.4
C_{HClO4}	
0.09 mol/L	99.7
0.11 mol/L	100.6
C_{HCl}	
0.0019 mol/L	99.9
0.0021 mol/L	100.4

* n=5.

Conclusion

DPASVA of selenium (IV) using ($GEM_{DDTC}N$) with an aqueous $HClO_4$ (0.1 M) and (0.002 M) HCl medium of pH 0.22 according to the optimal conditions was applied, liner calibration graph, $I_p=f(C_{Se^{4+}})$, were obtained in the concentration ranges of 1.974 -78.96 ng/mL with relative standard deviations (RSD)≤4.0%, the detection limit was 0.028 ng/mL on ($GEM_{DDTC}N$). 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 ($GEM_{DDTC}N$) was more sensitive and accurate than that obtained using bare gold, $GEM_{DAN}N$ and $GEM_{OPDA}N$ electrodes (the sensitivity was increased about 4000 times and about 2 times, respectively).

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