Determination of Se(IV) in Pharmaceuticals by Using Different Operating Modes of Pulse Anodic Stripping Voltammetric Analysis with Methylene Blue-Nafion Modified Gold Electrode

ABDUL AZIZ RAMADAN*, HASNA MANDIL and AMER OZOUN

Department of Chemistry, Faculty of Sciences, Aleppo University, Aleppo, Syria

*Corresponding authors: Fax: +963 21 2633136; E-mail: dramadan@scs-net.org; mandil@scs-net.org

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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 (PASVLA) and differential sampling on successive pulses ($\Delta I/\Delta t$) 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 ng mL^{-1} for operating modes PASVNP, PASVPP, PASVLA and $\Delta I/\Delta t$, 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.

Key Words: Selenium, Pharmaceuticals, Different operating modes of pulse anodic stripping voltammetry.

INTRODUCTION

The high tendency of 5-nitropiazselenol for self-accumulation on thin mercury film electrode was used innovatively for determination of Se(IV) in natural waters. 5-Nitropiazselenol was formed by reaction between Se(IV) and 4-nitro-1,2-phenylenediamine in acidic solution and self-accumulation process was carried out directly from reaction media. The adsorbed 5-nitropiazselenol was stripped in HCl solution by differential pulse cathodic potential scan. Detection limit of this method is 0.06 ng mL^{-1} . This method was applied for determination of Se(IV) in natural waters collected from some internationally registered lagoons south of Caspian Sea¹.

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 used the calibration curve².

A simple and fast cathodic stripping voltammetric procedure for determination of trace quantity of Se(IV) in natural samples containing high concentrations of surfactants and humic substances was developed. The procedure exploiting selenium accumulation {from sample solution spiked with 0.1 mol L^{-1} HClO_4 and 4×10^{-4} mol L^{-1} $\text{Cu}(\text{NO}_3)_2$ } as Cu_2Se was

employed as the initial method. The deposited Cu_2Se was stripped by differential pulse cathodic potential scan. The method was tested on synthetic samples spiked with surfactants and humic substances. The calibration graph for Se(IV) under optimized conditions following the accumulation of 30 s was linear in the range from 2×10^{-9} to 2×10^{-7} mol L^{-1} and was found to obey the equation $y = 0.74x - 0.61$, where y and x are the peak current (nA) and Se(IV) concentration (nmol L^{-1}), respectively. The linear correlation coefficient was $r = 0.9993$. The relative standard deviation for determination of Se(IV) at the concentration of 1×10^{-8} mol L^{-1} was 3.7 % ($n = 5$)³.

The suitability of a carbon paste electrode coupled with differential pulse voltammetry (DPV) has been investigated for the determination of Se(IV) after complexation with 2,3-diaminonaphthalene (2,3-DAN). A decrease of oxidation current of 2,3-diaminonaphthalene was observed due to the formation of a complex of 2,3-diaminonaphthalene with Se(IV). The calibration plots were linear in the range from 1 to 10 $\mu\text{g L}^{-1}$ with $r = 0.998$ and 10 to 100 $\mu\text{g L}^{-1}$ with $r = 0.998$. The relative standard deviation for five replicate analyses of 10 $\mu\text{g/L}$ of selenium was 2.5 %. The limit of detection was 0.7 $\mu\text{g L}^{-1}$. The voltammetric method was used for the determination of Se(IV) in tap water and pharmaceutical preparation. The results obtained by DPV method were validated by inductively coupled plasma optical emission spectroscopy (ICP-OES)⁴.

The behaviour of selenium(IV) at a mercury-film electrode previously modified with copper was studied by cathodic stripping voltammetry using an automatic system for replacing solutions without opening the circuit. The detection limit for selenium(IV) was found to be 40 ng L^{-1} ($5.0 \times 10^{-10} \text{ M}$) at an electrolysis time of 10 min^5 .

A simple micellar liquid chromatographic technique for the determination of selenium(IV) in pharmaceutical products (multi-vitamin tablets, syrups) and animal premixes after pre-column derivatization with 2,3-diaminonaphthalene was developed and validated. Hypersil ODS column, 10 % (v/v) 1-butanol in 0.05 M sodium dodecyl sulfate as the mobile phase and UV detection at 378 nm and were used. The retention time was about 8 min. In the course of the validation study, the specificity of the method was demonstrated. Linearity was established in the range $0.33\text{--}3.3 \text{ } \mu\text{g mL}^{-1}$ of selenium(IV) content. The limits of detection and quantitation were 0.1 and $0.3 \text{ } \mu\text{g mL}^{-1}$, respectively. The method showed excellent accuracy (100.04 %). Precision (repeatability) gave a relative standard deviation less than 1 %⁶.

A hydride generation method for the determination of traces of selenium at ng mL^{-1} concentration ranges has been introduced using a solid mixture of tartaric acid and sodium tetrahydroborate. Atomic absorption spectrometry has been used as the detection system. Several parameters such as the ratio of tartaric acid to sodium tetrahydroborate, type and amount of acid and the reaction temperature were optimized by using 640 ng mL^{-1} of Se(IV) standard solution. The calibration curve was linear from 20 to 1200 ng mL^{-1} . The relative standard deviation (% R.S.D.) of the determination was 1.93 % and the detection limit was 10.6 ng mL^{-1} . The reliability of the method was checked using different types of environmental samples, such as several types of water, a sample of soil and also in a kind of calcium phosphate sample by standard additions method⁷.

Differential pulse anodic stripping voltammetric (DPASV) determination of selenium(IV) using a vitamin E-nafion modified gold electrode ($V_{\text{E}}\text{NMGE}$) 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, $I_p = f(C_{\text{Se}^{4+}})$, was obtained in the concentration ranges of 5×10^{-8} to $1 \times 10^{-5} \text{ mol L}^{-1}$ with relative standard deviations (RSD) $\leq 4.5 \%$. This method shows that, the results for the determination of Se(IV) using $V_{\text{E}}\text{NMGE}$ were more sensitive and accurate than that obtained using bare gold electrode; the sensitivity was increased about 200 times⁸.

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 HClO_4 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 $1030\text{--}1060 \text{ mV}$. The calibration graph for Se(IV) under optimized conditions was linear in the range from 1×10^{-8} to $1 \times 10^{-6} \text{ mol L}^{-1}$ 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 ($\mu\text{mol L}^{-1}$ 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 $1 \times 10^{-8} \text{ mol L}^{-1}$ was 4.2 % ($n = 5$). The detection limit was $5.0 \times 10^{-9} \text{ mol L}^{-1}$. This method shows that, the results for the determination of Se(IV) using MBNMGE were more sensitive and accurate than that obtained using vitamin E-nafion modified gold electrode ($V_{\text{E}}\text{NMGE}$) about 5 times and about 1000 times using bare gold electrode⁸.

EXPERIMENTAL

A Metrohm 797 VA processor, A Metrohm 797 VA stand with a multi-mode electrode (MME), an auxiliary platinum electrode, a reference electrode (Ag/AgCl), the three-electrode cell and a polarographic analyser, model PRG-5 (Tacussel), for using different operating modes of pulse anodic stripping voltammetry (PASV): with constant amplitude of negative (PASVNP) or positive (PASVPP) polarity, imposed pulses of linearly increasing amplitude (PASVLIA) and imposed pulses of linearly increasing amplitude, with current measurement by means of differential sampling on successive pulses ($\Delta I/\Delta t$) were applied. A programmer model POLARMAX-78 and a recorder model ECOSRIPT (Tacussel) were also used. A rotating disk gold electrode (RDGE) model DI-65-14 (Tacussel) was used as a working modified gold electrode⁸. 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 $100 \text{ } \mu\text{L}$ sample syringe and five continuously adjustable pipettes covering a volume range from 20 to $5000 \text{ } \mu\text{L}$ (model PIPTMAN P, GILSON), were used for preparation of the experimental solutions.

Nafion perfluorinated ion-exchange resin (5 %) was purchased from Aldrich. Methylene blue, H_2SeO_3 and all other reagents were of analytical grade from Merck. A stock solution (a) $1 \times 10^{-4} \text{ mol L}^{-1}$ and stock solution (b) $1 \times 10^{-6} \text{ mol L}^{-1}$ of Se(IV) were prepared in 1.0 M HClO_4 . A working solutions for voltammetric investigations were prepared by dilution of the stock solutions (a or b) using 1.0 M HClO_4 .

A commercial formulations (tablet) were used for the analysis of Se(IV) by using different operating modes of PASV: with PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$ methods. The pharmaceutical formulations were used as the follows: Cenyt Silver, Pharmasyr Co.-Damascus-Syria, Each tablet contains: $20 \text{ } \mu\text{g}$ Selenium; Cenvite, Pharmasyr Co.-Damascus-Syria, Each tablet contains: $25 \text{ } \mu\text{g}$ Selenium; Ophtavite, Medipharma for Pharmaceutical Industries -Damascus-Syria, License No. 274 / 2001, Each tablet contains: $40 \text{ } \mu\text{g}$ Selenium; Supratech, MPI-Damascus-Syria, Licensed by: Roche Consumer Health-Switzerland, Each tablet contains: $55 \text{ } \mu\text{g}$ Selenium; Adavit Silver, Adamco Co.-Damascus-Syria, each tablet contains: $105 \text{ } \mu\text{g}$ 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 a solution of 1 M HClO_4 and filtered over a 100 mL flask and diluting to 100 mL with same

solution of HClO_4 . Five stock solutions of pharmaceuticals *i.e.*, cenyite silver, cenvite, ophtavite, supratch and adavit silver, which content: 600, 750, 1200, 1650 and 3150 ng mL^{-1} of Se(IV), respectively. Working solutions of pharmaceuticals were prepared by diluting: 4.167, 3.333, 2.084, 1.515 and 0.794 mL of stock solutions respectively to 100 mL with 1 M HClO_4 (each one content 25 ng mL^{-1} selenium). Working standard additions solutions of pharmaceuticals were prepared as the follows: same mentioned volumes of stock solutions of pharmaceuticals with 0.100, 0.200, 0.300, 0.500, 0.750 and 1.000 mL from stock solution (b) of selenium and diluting to 100 mL with 1.0 M HClO_4 ; each one content 25 ng mL^{-1} selenium (from pharmaceutical formulations) with 7.896, 15.792, 23.688, 39.48, 59.22 and 78.96 ng mL^{-1} selenium from standard additions solutions of Se(IV), respectively.

A 10 mL volume of a solution containing an appropriate concentration of selenium (from working solutions of selenium or working solutions of pharmaceuticals or working standard additions solutions of pharmaceuticals) was transferred into an electrochemical cell. The accumulation potential (-240 mV) was applied to the modified electrode for a certain time. The potential was then scanned from 0.0 to 1250 mV with the auto-scan facility by using different operating modes of PASV: PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$. The peak potential was measured at 1010-1140 mV. All results for pure Se(IV) were obtained using calibration curves and all results for pharmaceuticals were obtained using the method of standard additions.

RESULTS AND DISCUSSION

Voltammetric behaviour: The voltammograms (in the optimal conditions: composition of modified electrode, concentration HClO_4 , accumulation potential and accumulation time⁸) using a methylene blue-nafion modified gold electrode by different operating modes of pulse anodic stripping voltammetry (PASV): with PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$ were shoed in Fig. 1. The peak potential was measured at 1000-1010, 1030-1040, 1130-1140 and 1030-1060 mV for operating modes PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$, respectively. The optimum parameters established for studied different operating modes of pulse anodic stripping voltammetry showed in Table-1.

Calibration curves: Calibration curves for the determination of Se(IV) using a methylene blue-nafion modified gold electrode by different operating modes of PASV were studied. The peak current (I_p) was proportional to the concentration of Se(IV) over the ranges 7.896-78.96 ng mL^{-1} , ($y = 102.7x + 0.820$, $R^2 = 0.999$), 23.688-118.44 ng mL^{-1} , ($y = 8.081x + 3.025$, $R^2 = 0.993$), 23.688-118.44 ng mL^{-1} , ($y = 208.1x + 10.20$, $R^2 = 0.997$) and 0.7896-78.96 ng mL^{-1} , ($y = 145.8x + 0.645$, $R^2 = 0.999$; $y: I_p$, nA and $x: C_{\text{Se(IV)}}$, ng mL^{-1}) using PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$ respectively.

Analytical results: Determination of Se(IV) on the methylene blue-nafion modified electrode by different operating modes of PASV using analytical curves, $I_p = f(C_{\text{Se(IV)}})$, showed that the sensitivity increase according to the following operating modes: PASVPP, PASVLIA, PASVNP and $\Delta I/\Delta t$, respectively and the accuracy increase according to the

following operating modes: PASVPP, PASVLIA, $\Delta I/\Delta t$ and PASVNP, respectively (Table-2). Limit of detection and limit of quantitation for the determination of Se(IV) by different operating modes were applied. The volumes of limit of detection were as the followas : 0.89, 3.5, 3.4 and 0.11 ng mL^{-1} and the volumes of limit of quantitation were as the followas : 2.7, 10.6, 10.4 and 0.32 ng mL^{-1} using PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$, respectively.

Fig. 1. Determination of Se(IV) with a methylene blue-nafion modified gold electrode in 1.0 M HClO_4 by using different operating modes of PASV: (A): PASVNP: 1-electrolyte, 2-7.896, 3-15.792, 4-23.688, 5-39.48, 6-59.22 and 7-78.96 ng mL^{-1} $C_{\text{Se(IV)}}$; (B): PASVPP: 1-electrolyte, 2-23.688, 3-39.48, 4-59.22, 5-78.96 and 6-118.44 ng mL^{-1} $C_{\text{Se(IV)}}$; (C): PASVLIA: 1-electrolyte, 2-23.688, 3-39.48, 4-59.22, 5-78.96 and 6-118.44 ng mL^{-1} $C_{\text{Se(IV)}}$; (D): $\Delta I/\Delta t$: 1-electrolyte, 2-0.7896, 3-3.948, 4-7.896, 5-15.792, 6-23.688, 7-39.48, 8-59.22 and 9-78.96 ng mL^{-1} $C_{\text{Se(IV)}}$ (accumulation time 300s, accumulation potential -240 mV)

Applications: Many applications for the determination of Se(IV) in some Syrian pharmaceutical preparations with a methylene blue-nafion modified gold electrode in 1.0 M HClO_4 by using different operating modes of pulse anodic stripping voltammetry: with PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$ were proposed. Regression equations and correlation coefficients were included in Table-3. Standard additions curves for determination of selenium in different Syrian pharmaceutical preparations were used. The standard additions curves of cenyite silver by using mentioned operating modes were showed in Fig. 2, as an example. It was found that the pulse anodic stripping voltammetry with constant amplitude of negative polarity (PASVNP) method is the most accurate compared to the other studied methods. The amount of selenium in the sample (m) calculated from the following relationship: $m = h.m'$, where: m' is the amount of selenium in tablet ($\mu\text{g/tab.}$) calculated from the standard additions curve according to the following regression equation: $y = a.x + b$; when $y = 0$ is $m' = x = b/a = \text{intercept/slope}$ and h is (the stated amount of selenium

TABLE-1
OPTIMUM PARAMETERS ESTABLISHED FOR DETERMINATION OF Se (IV) WITH A METHYLENE BLUE-NAFION MODIFIED GOLD ELECTRODE IN 1.0 M HClO₄ BY USING DIFFERENT OPERATING MODES OF PULSE ANODIC STRIPPING VOLTAMMETRY

Parameters	Operating modes			
	PASVNP	PASVPP	PASVLIA	$\Delta I/\Delta t$
Accumulation (deposition) time	300 s			
Accumulation potential	-240 mV			
Supporting electrolyte	1.0 M HClO ₄			
Indicator electrode	Rotating disk gold electrode (RDGE)			
Modified electrode composition	1.2 mg mL ⁻¹ methylene blue and nafion 2 %,v/v ethanol			
Waiting time	5 s			
Initial potential	0.0 mV			
Final potential	+1250 mV			
Pulse duration	20 ms			
Scan rate	10 mV/s			
Stirring speed	1000 rpm			
Temperature of solution	25 ± 0.5 °C			
Peak Potential (mV)	1000-1010	1030-1040	1130-1140	1030-1060
LOD (3.3SD), ng mL ⁻¹	0.89	3.5	3.4	0.11
LOQ (10SD), ng mL ⁻¹	2.7	10.6	10.4	0.32
Linearity range, ng mL ⁻¹	7.896-78.96	23.688-118.44	23.688-118.44	0.7896-78.96
Regression equation:				
Slope	102.7	8.081	208.1	145.8
Intercept	0.82	3.025	10.20	0.645
Correlation coefficient (R ²)	0.999	0.993	0.997	0.999
RSD (%)	3.4	4.5	4.4	4.2

TABLE-2
DETERMINATION OF Se (IV) WITH A METHYLENE BLUE-NAFION MODIFIED GOLD ELECTRODE IN 1.0 M HClO₄ BY USING DIFFERENT OPERATING MODES OF PULSE ANODIC STRIPPING VOLTAMMETRY (ACCUMULATION TIME 300 s, ACCUMULATION POTENTIAL -240 mV)

Operating modes	x_i , ng mL ⁻¹ (taken)	$\bar{X}$ *, ng mL ⁻¹ (found)	SD, ng mL ⁻¹	$\frac{SD}{\sqrt{n}}$, ng mL ⁻¹	$\bar{x} \pm \frac{t \cdot SD}{\sqrt{n}}$ ng mL ⁻¹	RSD (%)
$\Delta I/\Delta t$	0.7896	0.782	0.032	0.014	0.782± 0.040	4.2
	1.5792	1.595	0.065	0.029	1.595± 0.081	4.1
	3.1584	3.158	0.13	0.059	3.158± 0.163	3.9
	3.948	3.948	0.15	0.067	3.948± 0.186	3.8
	7.896	7.975	0.28	0.125	7.975± 0.348	3.5
	15.792	15.713	0.52	0.232	15.713± 0.645	3.3
	23.688	23.688	0.76	0.340	23.688± 0.943	3.2
	39.48	39.48	1.18	0.528	39.48± 1.465	3.0
	59.22	54.96	1.50	0.671	54.96± 1.862	2.7
PASVNP	78.96	79.12	1.97	0.881	79.12± 2.446	2.5
	7.896	7.875	0.27	0.121	7.875± 0.335	3.4
	15.792	15.793	0.50	0.224	15.793± 0.621	3.1
	23.688	23.684	0.71	0.317	23.684± 0.881	3.0
	39.48	39.48	1.11	0.496	39.48± 1.378	2.8
	59.22	54.98	1.37	0.613	54.98± 1.701	2.5
PASVLIA	78.96	78.83	1.73	0.774	78.83± 2.148	2.2
	23.688	23.680	1.04	0.465	23.680± 1.291	4.4
	31.584	31.862	1.37	0.613	31.862± 1.701	4.3
	39.48	39.35	1.65	0.738	39.35± 2.048	4.2
	47.376	47.375	1.94	0.868	47.375 ± 2.408	4.1
	59.22	59.06	2.42	1.08	59.06± 3.004	4.1
	67.116	67.193	2.69	1.20	67.193± 3.340	4.0
PASVPP	78.96	78.87	3.07	1.37	78.87± 3.811	3.9
	118.44	118.40	4.38	1.96	118.40± 5.438	3.7
	23.688	23.687	1.06	0.474	23.687± 1.316	4.5
	39.48	39.42	1.93	0.863	39.42± 2.396	4.9
	47.376	47.375	2.23	0.997	47.375± 2.768	4.7
	59.22	59.18	2.72	1.22	59.18± 3.377	4.6
	67.116	67.23	2.96	1.32	67.23± 3.675	4.4
	78.96	78.99	3.40	1.52	78.99± 4.221	4.3
	98.70	98.53	4.14	1.85	98.53± 5.140	4.2
	118.44	118.52	4.86	2.17	118.52± 6.034	4.1

*n = 5, t = 2.776

TABLE 3
REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS FOR THE DETERMINATION OF Se(IV)
IN SOME SYRIAN PHARMACEUTICAL PREPARATIONS USING STANDARD ADDITIONS METHOD
BY USING DIFFERENT OPERATING MODES OF PASV ($m' = \text{INTERCEPT/SLOPE}$)

Pharmaceutical preparations	Operating modes			
	PASVNP	PASVPP	PASVLIA	$\Delta I/\Delta t$
Cenyite Silver 20 $\mu\text{g}/\text{tab.}$	$y = 102.7x + 2698$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 0.8 \text{ m'}$	$y = 8.08x + 213$ $R^2 = 0.993$ $m_{\text{Se(IV)/tbl.}} = 0.8 \text{ m'}$	$y = 208.3x + 5470$ $R^2 = 0.997$ $m_{\text{Se(IV)/tbl.}} = 0.8 \text{ m'}$	$y = 145.8x + 3843$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 0.8 \text{ m'}$
Cenvite 25 $\mu\text{g}/\text{tab.}$	$y = 102.6x + 2642$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = m'$	$y = 8.10x + 210$ $R^2 = 0.993$ $m_{\text{Se(IV)/tbl.}} = m'$	$y = 208.3x + 5365$ $R^2 = 0.997$ $m_{\text{Se(IV)/tbl.}} = m'$	$y = 146.0x + 3755$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = m'$
Ophtavite 40 $\mu\text{g}/\text{tab.}$	$y = 102.7x + 2722$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 1.6 \text{ m'}$	$y = 8.09x + 216$ $R^2 = 0.993$ $m_{\text{Se(IV)/tbl.}} = 1.6 \text{ m'}$	$y = 208.4x + 5568$ $R^2 = 0.997$ $m_{\text{Se(IV)/tbl.}} = 1.6 \text{ m'}$	$y = 145.8x + 3841$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 1.6 \text{ m'}$
Supratech 55 $\mu\text{g}/\text{tab.}$	$y = 103.0x + 2755$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 2.2 \text{ m'}$	$y = 8.08x + 216$ $R^2 = 0.993$ $m_{\text{Se(IV)/tbl.}} = 2.2 \text{ m'}$	$y = 208.2x + 5544$ $R^2 = 0.997$ $m_{\text{Se(IV)/tbl.}} = 2.2 \text{ m'}$	$y = 145.7x + 3864$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 2.2 \text{ m'}$
Adavit Silver 105 $\mu\text{g}/\text{tab.}$	$y = 102.8x + 2759$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 4.2 \text{ m'}$	$y = 8.09x + 218$ $R^2 = 0.993$ $m_{\text{Se(IV)/tbl.}} = 4.2 \text{ m'}$	$y = 208.1x + 5590$ $R^2 = 0.997$ $m_{\text{Se(IV)/tbl.}} = 4.2 \text{ m'}$	$y = 146.0x + 3723$ $R^2 = 0.999$ $m_{\text{Se(IV)/tbl.}} = 4.2 \text{ m'}$

in the sample, $\mu\text{g}/\text{tab.}$)/25. The results of quantitative analysis for Se(IV) in the pharmaceutical preparations using PASVNP method were calculated by the standard additions method, (Table-4).

Fig. 2. $I_p = f(C_{\text{Se(IV)}})$ for determination of Se (IV) in Syrian pharmaceutical preparations (cenyite silver) with a methylene blue-nafion modified gold electrode by using different operating modes of pulse anodic stripping voltammetry: (A) PASVNP; (B) PASVPP; (C) PASVLIA and (D) $\Delta I/\Delta t$ (accumulation time 300 s, accumulation potential -240 mV, y: I_p , nA and x: $C_{\text{Se(IV)}}$, ng mL⁻¹)

Conclusion

Determination of Se(IV) in Syrian pharmaceuticals with a methylene blue-nafion modified gold electrode by using different operating modes of PASV: with PASVNP, PASVPP, PASVLIA and $\Delta I/\Delta t$ was applied. Se(IV) was determined in an aqueous HClO_4 medium (1.0 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

TABLE-4
DETERMINATION OF Se(IV) IN SOME SYRIAN PHARMACEUTICAL PREPARATIONS USING STANDARD ADDITIONS METHOD BY USING PASVNP METHOD

Commercial name	Contents	$\bar{x}$ $\mu\text{g}/\text{tab}$	RSD (%)	Recovery (%)
Cenyite Silver, Ctd. tab. Pharmasyr Co. Damascus-SYRIA	20 $\mu\text{g}/\text{tab}$	21.01	3.6	105.05
Cenvite, Ctd. tab. Pharmasyr Co. Damascus-SYRIA	25 $\mu\text{g}/\text{tab}$	25.75	3.6	103.00
Ophtavite, Ctd. tab. Medipharma for pharmaceutical industries Damascus-SYRIA	40 $\mu\text{g}/\text{tab}$	42.41	3.1	106.03
Supratech, Ctd. tab. MPI Damascus-SYRIA	55 $\mu\text{g}/\text{tab}$	58.85	3.3	107.00
Adavit Silver, Ctd. tab. Adamco co. Damascus-SYRIA	105 $\mu\text{g}/\text{tab}$	107.40	3.0	102.29

facility. The peak potential was measured at 1000-1010, 1030-1040, 1130-1140 and 1030-1060 mV and the calibration graph 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 ng mL⁻¹ for operating modes (PASVNP), (PASVPP), (PASVLIA) and ($\Delta I/\Delta t$), respectively. RSD % was less than 5.

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