



## Differential Pulse Anodic Stripping Voltammetric Determination of Selenium(IV) with A Methylene Blue-Nafion Modified Gold Electrode

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(Received: 8 January 2011;

Accepted: 24 September 2011)

AJC-10442

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<sub>4</sub> medium (1.0 M) at an accumulation potential of -240 mV and an accumulation time of 300 s. The potential was then scanned from 0.0 to 1250 mV by differential pulse anodic stripping voltammetry using the auto-scan facility. The peak height was measured at 1030-1060 mV. The calibration graph for Se(IV) under optimized conditions was linear in the range from  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  mol L<sup>-1</sup> (0.79 ng mL<sup>-1</sup> to 79 ng mL<sup>-1</sup>) and was found to obey the equation  $y = 11.50x + 0.003$ , where  $y$  and  $x$  are the peak current ( $\mu$ A) and Se(IV) concentration ( $\mu$ mol L<sup>-1</sup> or  $\mu$ M), respectively. The coefficient of determination was  $R^2 = 0.999$ . The relative standard deviations (RSD) for determination of Se(IV) at the concentration of  $1 \times 10^{-8}$  mol L<sup>-1</sup> was 4.2 % ( $n = 5$ ). The detection limit was  $5.0 \times 10^{-9}$  mol L<sup>-1</sup>. This method shows that the results for the determination of Se(IV) using methylene blue-Nafion modified gold electrode were more sensitive and accurate than that obtained using vitamin E-Nafion modified gold electrode (V<sub>E</sub>NMGE) about 5 times and about 1000 times using bare gold electrode.

**Key Words:** Methylene blue, Nafion, Modified gold electrode, Selenium, Determination, Differential pulse anodic stripping voltammetry.

### INTRODUCTION

Differential pulse anodic stripping voltammetric (DPASV) determination of selenium(IV) using a vitamin E-Nafion modified gold electrode (V<sub>E</sub>NMGE) has been studied. Selenium(IV) was determined in an aqueous HClO<sub>4</sub> medium of pH 1.10 at an accumulation potential of -240 mV and an accumulation time of 300 s. Under the optimum conditions, linear calibration graph,  $I_p = f(C_{Se^{4+}})$ , was obtained in the concentration ranges of  $5 \times 10^{-8}$  to  $1 \times 10^{-5}$  mol L<sup>-1</sup> with relative standard deviations (RSD) 4.5 %. This method shows that, the results for the determination of Se(IV) using V<sub>E</sub>NMGE were more sensitive and accurate than that obtained using bare gold electrode and the sensitivity was increased about 200 times<sup>1</sup>.

Determination of Se(IV) by pulse anodic stripping voltammetry with constant amplitude of negative polarity (SVPNP) using a V<sub>E</sub>NMGE has been studied. Selenium(IV) was determined in an aqueous HClO<sub>4</sub> medium (pH = 1.10) at an accumulation potential of -240 mV and an accumulation time of 300 s. The analytical signal was linear from in the concentration ranges of  $1 \times 10^{-7}$  to  $8 \times 10^{-6}$  mol L<sup>-1</sup> with relative standard deviations (RSD) 5.2 %<sup>2</sup>.

The performance of a poly(1,8-diaminonaphthalene)-modified gold electrode (pDAN-Au) for the determination of the selenium(IV) ion in an acidic aqueous medium was investigated with anodic stripping differential pulse voltammetry. The detection limit was  $9.0 \times 10^{-9}$  M for Se(IV) with 4.4 % of RSD<sup>3</sup>.

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<sup>-1</sup>, but selenium was determined in the range 8 to 64 ng mL<sup>-1</sup> in pharmaceutical products used the calibration curve<sup>4</sup>.

Differential pulse voltammetric determination of selenocystine (SeC) using selenium-gold film modified glassy carbon electrode (Se-Au)/GC is presented. Selenocystine yields a sensitive reduction peak at -740 mV on (Se-Au)/GC electrode. The peak current has a linear relationship with the concentration of SeC in the range of  $5.0 \times 10^{-8}$  to  $7.0 \times 10^{-4}$  mol L<sup>-1</sup> in 0.10 mol L<sup>-1</sup> KNO<sub>3</sub> (pH 3.20) solution<sup>5</sup>.

Determination of Se(IV) was investigated on 3,3'-diaminobenzidine/Nafion/mercury film modified glass carbon electrode (DNMFE). Selenium(IV) was preconcentrated onto the

DNMFE from the sample solution saturated with ethylenediaminetetraacetate (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  $300 \text{ mg L}^{-1}$  with 5 min accumulation<sup>6</sup>.

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. The adsorbed 5-nitropiazselenol was stripped in HCl solution by DP cathodic potential scan. Detection limit of this method is  $0.06 \text{ ng mL}^{-1}$ . This method was applied for determination of Se(IV) in natural waters collected from some internationally registered lagoons south of Caspian sea<sup>7</sup>.

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  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$  and  $4 \times 10^{-4} \text{ mol L}^{-1} \text{ Cu}(\text{NO}_3)_2$ ] as  $\text{Cu}_2\text{Se}$  was employed as the initial method. 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  $2 \times 10^{-9}$  to  $2 \times 10^{-7} \text{ mol L}^{-1}$  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 ( $\text{nmol L}^{-1}$ ), respectively. The linear correlation coefficient was  $r = 0.9993$ . The relative standard deviation for determination of Se(IV) at the concentration of  $1 \times 10^{-8} \text{ mol L}^{-1}$  was 3.7% ( $n = 5$ )<sup>8</sup>.

A simple and rapid stripping voltammetric method is described for the determination of selenium, copper, lead and cadmium in a single sample solution. The method utilizes differential pulse cathodic stripping voltammetry for the determination of selenium and differential pulse anodic stripping voltammetry for the other three elements. The use of a deposition potential of  $-0.3$  V vs. SCE allows the determination of selenium in the presence of interfering ions at 1000-fold concentrations. Subsequent oxidation of the selenium to the electro-inactive selenium(VI) permits direct determination of the other three elements in the same solution. The limits of detection obtained by this method were  $0.1 \text{ } \mu\text{g L}^{-1}$  for selenium,  $0.5 \text{ } \mu\text{g L}^{-1}$  for copper and  $0.01 \text{ } \mu\text{g L}^{-1}$  for lead and cadmium<sup>9</sup>.

A simple, reproducible and low cost method, employing differential pulse anodic stripping voltammetry, for determination of selenium(IV) with a gold electrode obtained from recordable compact disks (CD-R) were used to evaluate the voltammetric behaviour of the metallic ion in  $0.1 \text{ mol L}^{-1} \text{ HClO}_4$ . To evaluate the voltammetric behaviour of Se(IV), parameters such as deposition potential and deposition time were optimized. A wide linear response range, from 0.5 to  $291 \text{ ng mL}^{-1}$ , was obtained using a 5.0 mm diameter gold electrode<sup>10</sup>.

## EXPERIMENTAL

Nafion perfluorinated ion-exchange resin (5 %) was purchased from Aldrich. Methylene blue,  $\text{H}_2\text{SeO}_3$  and all other reagents were of analytical grade from Merck. A stock solution ( $0.01 \text{ mol L}^{-1}$ ) of Se(IV) was prepared using deionized water. An  $\text{HClO}_4$  solution 1.0 M was used. A working solution for

voltammetric investigations was prepared by dilution of the stock solution with  $\text{HClO}_4$  solution. All results were obtained using calibration curves.

A polarographic 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 (Tacussel) 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  $25 \text{ }^\circ\text{C}$ . 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.

**Preparation of modified gold electrode:** Prior to each experiment, the Au electrode was first polished, rinsed with deionized water and ultrasonicated successively in a 1:1 aqueous solution of nitric acid and an ethanol solution each for 2 min. It was then dried. A modified solution was prepared by putting 3 mL of methylene blue ( $4 \text{ mg mL}^{-1}$ ) and 2 mL of Nafion-ethanol 10 % (v/v) solution in 10 mL volumetric flask, then the volume was diluted to the mark with ethanol ( $1.2 \text{ mg mL}^{-1}$  methylene blue and 2 %, v/v Nafion). A modified Au electrode was prepared by placing modified solution onto the dry electrode with a micro syringe. The electrode was dried to evaporate the solvent and rinsed with deionized water, then it was applied potential at  $+1240$  mV during 15 min.

**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 ( $-240$  mV) was applied to the modified electrode for a certain time. The potential was then scanned from 0.0 to 1250 mV by differential pulse anodic stripping voltammetry using the auto-scan facility. The peak height was measured at 1030-1060 mV.

## RESULTS AND DISCUSSION

**Voltammetric behaviour:** The differential pulse anodic stripping voltammograms using the procedure described above with a bare Au electrode ( $C_{\text{Se(IV)}} \geq 1 \times 10^{-4} \text{ mol L}^{-1}$ , RSD = 6.8 %) and the sensitivity increased 200 times ( $C_{\text{Se(IV)}} \geq 5 \times 10^{-8} \text{ mol L}^{-1}$ , RSD = 4.5 %) an electrode modified with vitamin E-Nafion ( $\text{V}_\text{E}\text{NMGE}$ )<sup>1</sup>, while using a gold electrode modified with methylene blue-Nafion (MBNMGE), show that the peak potential shifted slightly from 1030 to 1060 mV and the sensitivity ( $C_{\text{Se(IV)}} \geq 1 \times 10^{-8} \text{ mol L}^{-1}$ , RSD = 4.2 %) increases 200 times compared with the use of  $\text{V}_\text{E}\text{NMGE}$  (Fig. 1).

**Effect of modified electrode composition:** The effect of the Nafion and methylene blue concentrations on the peak current were studied. The peak current reached its maximum when the concentration of Nafion is 2 %, v/v and methylene blue is  $1.2 \text{ mg mL}^{-1}$ .

**Effect of concentration  $\text{HClO}_4$ :** The influence of concentration  $\text{HClO}_4$  was analyzed with the response of the peak current. The dependence of peak current ( $I_p$ ) with concentration  $\text{HClO}_4$

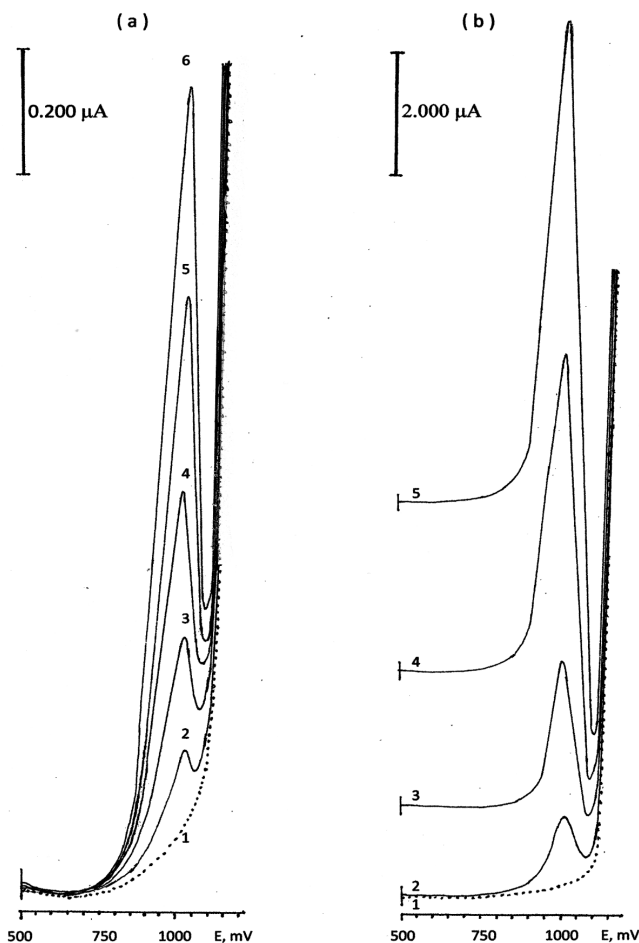


Fig. 1. Differential pulse anodic stripping voltammograms of Se(IV) on methylene blue-Nafion modified gold electrode in 1.0 M HClO<sub>4</sub>: (a) C<sub>Se(IV)</sub>: (1) electrolyte, (2)  $1.0 \times 10^{-8}$ , (3)  $2.5 \times 10^{-8}$ , (4)  $5.0 \times 10^{-8}$ , (5)  $7.5 \times 10^{-8}$  and (6)  $1.0 \times 10^{-7}$  M, (b) C<sub>HClO<sub>4</sub></sub>: (1) electrolyte, (2)  $1.0 \times 10^{-7}$ , (3)  $2.0 \times 10^{-7}$ , (4)  $6.0 \times 10^{-7}$ , (5)  $1.0 \times 10^{-6}$  M. (accumulation time 300 s, accumulation potential -240 mV).

solution was studied. Fig. 2 shows that, the maximum of  $I_p$  using differential pulse anodic stripping voltammetric (DPASV) analysis for  $1 \times 10^{-7}$  mol L<sup>-1</sup> (0.1 μM) of Se(IV) on methylene blue-Nafion modified gold electrode (MBNMGE) was at 1.0 M.

**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 -240 mV.

**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. At concentration ranges of  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  mol L<sup>-1</sup> of Se(IV), the current is nearly linear from 250 to 350 s. We have studied the factors that affected in peak current, *i.e.*, accumulation time, accumulation potential, concentration of HClO<sub>4</sub>, modified electrode composition. Also, the influence of pulse duration, waiting time, initial potential, final potential, stirring speed, scan rate and temperature of solution onto sensitivity of the determination of selenium was studied. Finally, the optimum parameters for DPASV determination of selenium(IV) using DPASV method at MBNMGE were selected and presented in the Table-1.

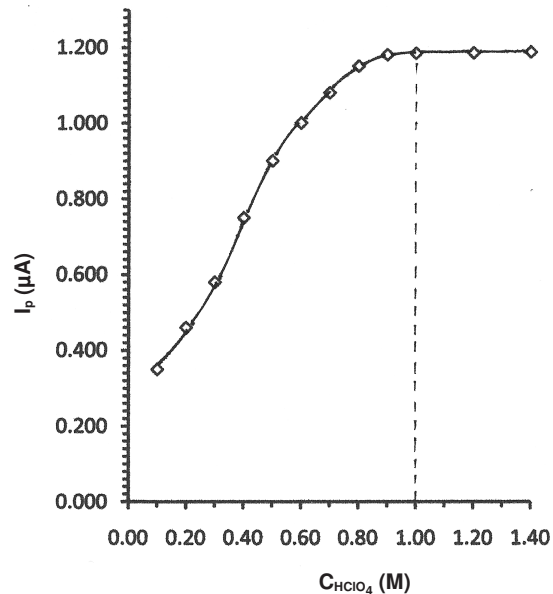


Fig. 2. Effect of concentration of HClO<sub>4</sub> on differential pulse anodic stripping voltammograms of Se(IV) using methylene blue-Nafion modified gold electrode (accumulation time 300 s, accumulation potential -240 mV and C<sub>Se(IV)</sub> =  $1.0 \times 10^{-7}$  M)

TABLE-1  
OPTIMUM PARAMETERS ESTABLISHED  
FOR DIFFERENTIAL PULSE ANODIC STRIPPING  
VOLTAMMETRIC DETERMINATION OF SELENIUM (IV)

Accumulation (deposition) time (s)	300
Accumulation potential (mV)	-240
Supporting electrolyte	1 M HClO <sub>4</sub>
Indicator electrode	Rotating disk gold electrode
Modified electrode composition	1.2 mg mL <sup>-1</sup> methylene blue and Nafion 2%, v/v ethanol
Waiting time (s)	5
Initial potential (mV)	0.0
Final potential (mV)	+1250
Pulse duration (ms)	20
Scan rate (mV/s)	10
Stirring speed (rpm)	1000
Temperature of solution (°C)	25 ± 0.5

**Analytical results:** The analytical curves,  $I_p = f(C_{\text{Se(IV)}})$  for the determination of Se(IV) in presence of 1.0 M HClO<sub>4</sub> on the methylene blue-Nafion modified electrode by differential pulse anodic stripping voltammetric analysis showed linear proportionality over the concentration range from  $1 \times 10^{-8}$  to  $1 \times 10^{-6}$  M (Fig. 3) 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 (μM or μmol L<sup>-1</sup>), respectively. In this method we determined a very low concentration ( $1 \times 10^{-8}$  M) of Se(IV), 0.79 ng mL<sup>-1</sup>, on the methylene blue-Nafion modified gold electrode in presence of 1.0M HClO<sub>4</sub> with relative standard deviation not exceed ± 4.2 % (Table-2). The detection limit was  $5.0 \times 10^{-9}$  M. This method gives accurate and sensitive results compared with references.

## Conclusion

Trace level of selenium(IV) was determined by differential pulse anodic stripping voltammetric analysis in a aqueous HClO<sub>4</sub> medium (1.0 M) using a methylene blue-Nafion modified gold electrode at an accumulation potential of -240 mV

TABLE-2  
DETERMINATION OF SELENIUM(IV) BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRIC ANALYSIS IN PRESENT 1 M OF HClO<sub>4</sub> ON A METHYLENE BLUE-NAFION MODIFIED GOLD ELECTRODE (ACCUMULATION TIME 300 s, ACCUMULATION POTENTIAL -240 mV)

$x_i$ , $\mu\text{M}$ (taken)	$\bar{x}^*$ , $\mu\text{M}$ (found)	SD ( $\mu\text{M}$ )	$\frac{SD}{\sqrt{n}}$ , $\mu\text{M}$	$\bar{x} \pm \frac{t \cdot SD}{\sqrt{n}}$ , $\mu\text{M}$	RSD (%)
0.0100	0.0099	0.00041	0.00018	$0.0099 \pm 0.00050$	4.2
0.0150	0.0150	0.00063	0.00028	$0.0150 \pm 0.00078$	4.2
0.0200	0.0202	0.00082	0.00037	$0.0202 \pm 0.00103$	4.1
0.0300	0.0298	0.00120	0.00054	$0.0298 \pm 0.00150$	4.0
0.0400	0.0400	0.00160	0.00071	$0.0400 \pm 0.00200$	3.9
0.0500	0.0500	0.00190	0.00085	$0.0500 \pm 0.00240$	3.8
0.1000	0.1010	0.00350	0.00160	$0.1010 \pm 0.00440$	3.5
0.2000	0.1990	0.00660	0.00290	$0.1990 \pm 0.00810$	3.3
0.3000	0.3000	0.00960	0.00430	$0.3000 \pm 0.01200$	3.2
0.4000	0.4020	0.01200	0.00540	$0.4020 \pm 0.01500$	3.1
0.5000	0.5000	0.01500	0.00670	$0.5000 \pm 0.01900$	3.0
0.6000	0.5970	0.01700	0.00760	$0.5970 \pm 0.02100$	2.9
0.7000	0.6960	0.01900	0.00850	$0.6960 \pm 0.02400$	2.8
0.8000	0.8000	0.02200	0.00980	$0.8000 \pm 0.02700$	2.7
0.9000	0.9040	0.02300	0.01030	$0.9040 \pm 0.02800$	2.6
1.0000	1.0020	0.02500	0.01120	$1.0020 \pm 0.03100$	2.5

\* $n = 5$ ,  $t = 2.776$ .

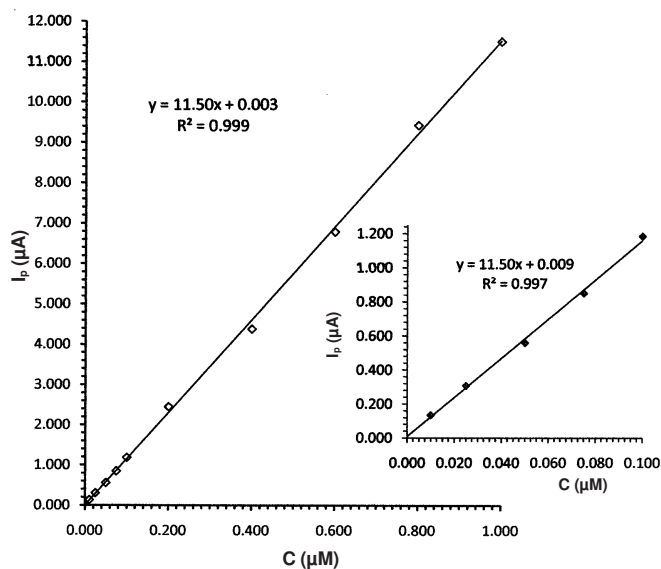


Fig. 3.  $I_p = f(C_{\text{Se(IV)}})$  for the determination of Se(IV) in presence of 1.0 M HClO<sub>4</sub> by differential pulse anodic stripping voltammetric analysis using a methylene blue-Nafion modified gold electrode (accumulation time 300 s, accumulation potential -240 mV, y:  $I_p$ , mA and x:  $C_{\text{Se(IV)}}$ , mM)

and an accumulation time of 300 s. Linear calibration graph,  $I_p = f(C_{\text{Se}^{4+}})$ , was obtained in the concentration ranges of  $1 \times 10^{-8}$

to  $1 \times 10^{-6}$  mol L<sup>-1</sup> ( $0.79 \text{ ng mL}^{-1}$  to  $79 \text{ ng mL}^{-1}$ ) with relative standard deviations (RSD) 4.2%. The detection limit was  $5.0 \times 10^{-9}$  M. This method shows that, the results for the determination of Se(IV) using MBNMGE were more sensitive and accurate than that obtained using V<sub>E</sub>NMGE about 5 times and about 1000 times using bare gold electrode.

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