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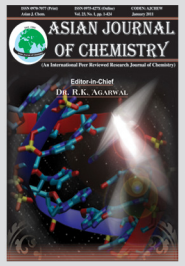

Differential Pulse Anodic Stripping Voltammetric Determination of Selenium(IV) With a Vitamin E-Nafion Modified Gold Electrode

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

Key Words: Vitamin E, Nafion, Selenium, Determination, Differential pulse anodic stripping voltammetry.

INTRODUCTION

The performance of a poly(1,8-diaminonaphthalene) (*p*DAN) modified electrode 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 experimental parameters for the analysis of selenium(IV) were optimized and the characteristics of this polymer-modified electrode were investigated by using cyclic voltammetry. The Se(IV) ions were chemically deposited onto the surface of the *p*DAN-Au electrode in an acidic medium. The detection limit employing the anodic stripping differential pulse voltammetry was 9×10^{-9} M for Se(IV) with 4.4 % of RSD[1].

Differential pulse cathodic stripping voltammetric determination of selenium from pharmaceutical products was applied. First, established the optimum parameters (electrolyte, deposition time, pulse duration, pulse amplitude, *etc*.) and second, the content of selenium was determined in five pharmaceutical products. The drug samples were treated with a mixture of 6 mL HNO_3 and 1 mL H_2O_2 in the microwave oven. The peak potential is -0.545 V *versus* Ag/AgCl and the calibration curve is linear up to 0.125 ng mL^{-1}, but selenium was determined in the range 8-64 ng mL^{-1} in pharmaceutical products used the calibration curve[2].

A method for the improvement of the signal-to-noise ratio in square-wave (SW) voltammetry is proposed. This method is applied to cathodic stripping voltammetric (CSV) determination of selenium(IV) in nitric acid solutions. Hanging mercury drop electrode (HMDE) was used in presence of the Cu(II) ions. The optimal conditions were chosen: square-wave waveform mode, pH, time and potential of electrodeposition. Kinetic processes of copper selenide reduction with the use of SWCSV, applying different squarewave waveforms, are studied. The standard reaction rate constants are evaluated for different square-wave waveforms. It is shown that the determination of Se(IV) by this modified SWCSV technique is possible with an excellent sensitivity (the detection limit 8×10^{-12} mol L^{-1} only for 5 min of electrodeposition) and good reproducibility (RSD < 8 %) in a wide range of concentration (1×10^{-11}-1×10^{-6} mol L^{-1}) of Se(IV)[3].

Differential pulse voltammetric determination of selenocystine (SeC) using selenium-gold film modified glassy carbon electrode (Se-Au)/GC is presented. In 0.10 mol L^{-1} KNO_3 (pH 3.20) solution, 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 selenocystine in the range of 5×10^{-8}-7×10^{-4} mol L^{-1}. The content of selenocystine in the selenium-enriched yeast and selenium-enriched tea is determined. A little amount of selenium is utilized by drinking tea and most selenium still stay in tealeaf. Uncertainty are 22.4 and 16.1 % for determination of selenocystine in selenium-enriched yeast and selenium-enriched tea by differential pulse voltammetry (DPV) on (Se-Au)/GC electrode, respectively[4].

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. Selenium(IV) was preconcentrated onto the DNMFE from the sample solution staturated 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 1-300 μg L^{-1} with 5 min accumulation[5].

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. All parameters influencing the measurement were optimized and evaluated. 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 registrated lagoons south of Caspian sea[6].

Determination of Se^{4+} by pulse anodic stripping voltammetry with constant amplitude of negative polarity (SVPNP) using a vitamin E-nafion modified gold electrode has been studied. Selenium(IV) was determined in an aqueous $HClO_4$ medium (pH = 1.1) at an accumulation potential of -240 mV and an accumulation time of 300 s. The analytical signal was linear in the concentration ranges of 1×10^{-7}-8×10^{-6} mol L^{-1} with relative standard deviations (RSD) ≤ 5.20 %[7].

EXPERIMENTAL

Nafion perfluorinated ion-exchange resin (5 %) was purchased from Aldrich. Vitamin E was from Basf/Germany. H_2SeO_3 and all other reagents were of analytical grade from Merck. A stock solution (0.01 mol L^{-1}) of Se(IV) was prepared using deionized water. An $HClO_4$ solution 0.10 M was used at pH = 1.10. A working solution for voltammetric investigations was prepared by dilution of the stock solution with $HClO_4$ solution. All results were obtained using calibration curves.

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 ºC. The diluter pipette model DIP-1 (Shimadzu), having 100 μL sample syringe and five continuously adjustable pipettes covering a volume range from 20-5000 mL (model PIPTMAN P, GILSON), were used for preparation of the experimental solutions.

Preparation of modified gold electrode: Prior to each experiment, the 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 2 min. It was then dried. A modified solution was prepared by putting 5 mL of vitamin E (1 mg mL^{-1}) and 5 mL of nafion-ethanol 10 % (v/v) solution in 25 mL volumetric flask, then the volume was diluted to the mark with ethanol (0.2 mg mL^{-1} vitamin E and 2 %, v/v nafion). A modified gold 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.

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 (-0.240 V) was applied to the modified electrode for a certain time. The potential was then scanned from 0.500-1.300 V by differential pulse anodic stripping voltammetry using the autoscan facility. The peak height was measured at 1.020-1.030 V.

RESULTS AND DISCUSSION

Voltammetric behaviour: The differential pulse anodic stripping voltammograms using the procedure described above with a bare Au electrode ($C_{Se(IV)} \geq 1 \times 10^{-4}$ mol L^{-1}, RSD = 6.8 %), while an electrode modified with vitamin E-nafion show that the peak potential shifted slightly from 1.020-1.030 V and the sensitivity increased ($C_{Se(IV)} \geq 5 \times 10^{-8}$ mol L^{-1}) when the vitamin E-nafion was introduced to modify the coating (Fig. 1).

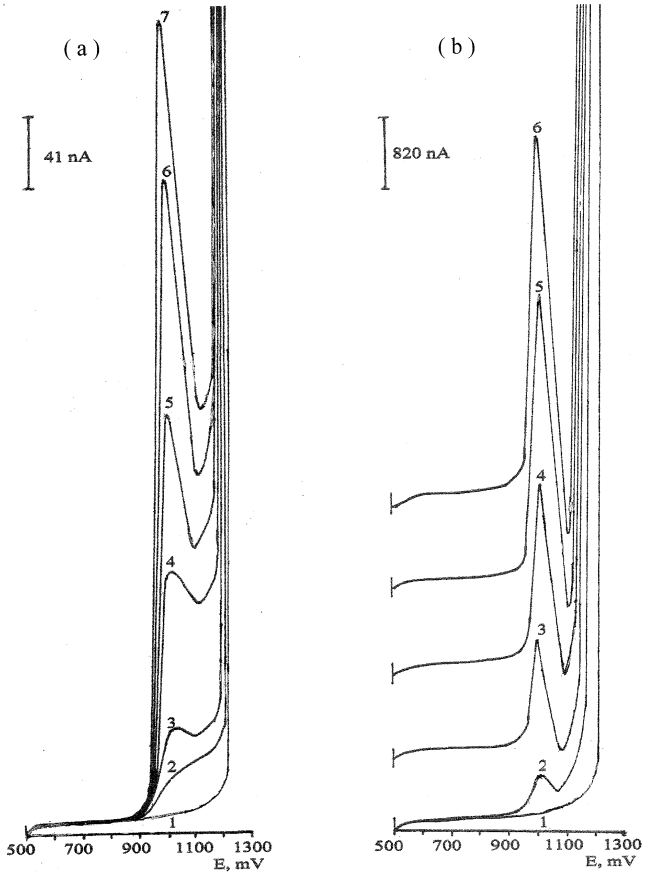

Fig. 1. Differential pulse anodic stripping voltammograms of Se(IV) on vitamin E-nafion modified gold electrode at pH 1.10 (0.10 M $HClO_4$): (a) $C_{Se(IV)}$: (1) electrolyte, (2) 5×10^{-8}, (3) 1×10^{-7}, (4) 3×10^{-7}, (5) 5×10^{-7}, (6) 8×10^{-7} and (7) 1×10^{-6} M. (b) $C_{Se(IV)}$: (1) electrolyte, (2) 1×10^{-6}, (3) 3×10^{-6}, (4) 5×10^{-6}, (5) 8×10^{-6}, (6) 1×10^{-5} M (accumulation time 300 s, accumulation potential -240 mV)

Effect of modified electrode composition: The effect of the nafion and vitamin E concentrations on the peak current were studied. The peak current reached its maximum when the concentration of nafion is 2 %, v/v and vitamin E is 0.2 mg mL^{-1}. When the concentration of nafion exceeded 2 %, the film became thicker and the electrical resistance became higher. This is due to the formation of a complex between vitamin E and Se(IV)[8].

Effect of pH: The influence of the solution $HClO_4$ (pH 0.80-4.50) was analyzed with the response of the peak current. The dependence of peak current (I_p) with pH solution was studied. Fig. 2 shows that, the maximum of I_p using differential pulse anodic stripping voltammetric (DPASV) analysis for 1×10^{-6} mol L^{-1} (1 μM) of Se(IV) on vitamin E-nafion modified gold electrode (V_ENMGE) was at pH 1.10.

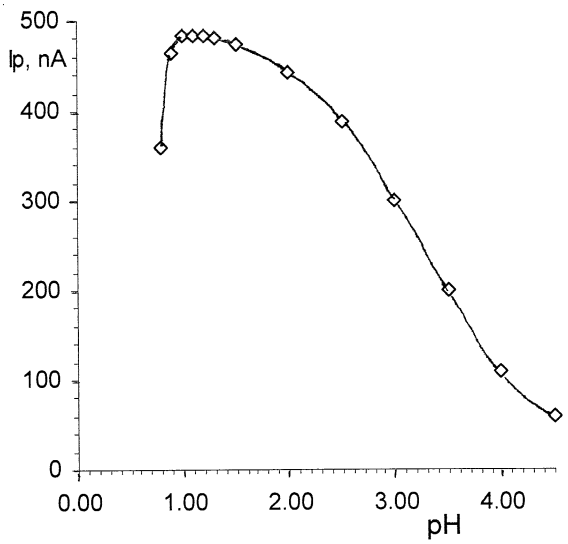

Fig. 2. Effect of pH on differential pulse anodic stripping voltammograms of Se(IV) using vitamin E-nafion modified gold electrode (accumulation time 300 s, accumulation potential -240 mV)

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 -0.240 V.

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 5×10^{-8}-1×10^{-5} mol L^{-1} of Se(IV), the current is nearly linear from 280-320 s. We have studied the factors that affected in peak current, *i.e.*, accumulation time, accumulation potential, pH value, 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) were selected and presented in the Table-1.

Analytical results: The analytical curevs, $I_p = f(C_{Se(IV)})$ for the determination of Se(IV) in presence of 0.10 M $HClO_4$ on the modified electrode by differential pulse anodic stripping voltammetric analysis showed linear proportionality over the concentration range from 5×10^{-8}-1×10^{-5} M (Fig. 3). In this method we determined a very low concentration (5×10^{-8} M) of Se(IV) on the vitamin E-nafion modified gold electrode in presence of 0.10 M $HClO_4$ with relative standard deviation not exceed ± 4.5 % (Table-2). This method gives accurate and sensitive results compared with references.

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	0.10 M $HClO_4$
Indicator electrode	Rotating disk gold electrode (RDGE)
pH solution	1.10
Modified electrode composition	0.2 mg mL^{-1} vitamin E and 2 %, v/v nafion-ethanol
Waiting time (s)	5
Initial potential (mV)	+ 500
Final potential (mV)	+ 1300
Pulse duration (ms)	20
Scan rate (mV/s)	10
Stirring speed (rpm)	1000
Temperature of solution (ºC)	25.0 ± 0.5

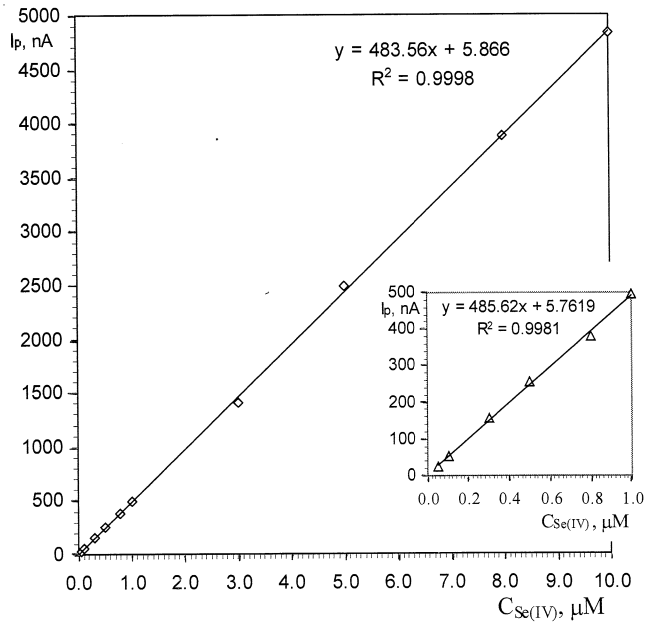

Fig. 3. $I_p = f(C_{Se(IV)})$ for the determination of Se(IV) in presence of 0.10 M $HClO_4$ by differential pulse anodic stripping voltammetric analysis using a vitamin E-nafion modified gold electrode (accumulation time 300 s, accumulation potential -240 mV, y: I_p, nA and x: $C_{Se(IV)}$, μM)

Conclusion

Trace level of selenium(IV) was determined by differential pulse anodic stripping voltammetric analysis in an aqueous $HClO_4$ medium of pH 1.10 using a vitamin E-nafion modified gold electrode at an accumulation potential of -240 mV and an accumulation time of 300 s. Liner calibration graph, $I_p = f(C_{Se^{4+}})$, was obtained in the concentration ranges of 5×10^{-8}-1×10^{-5} mol L^{-1} with relative standard deviations (RSD) ≤ 4.5 %.

TABLE-2
DETERMINATION OF SELENIUM(IV) BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRIC ANALYSIS IN PRESENCE OF 0.10 M $HClO_4$ (pH 1.10) ON A VITAMIN E-NAFION MODIFIED GOLD ELECTRODE (ACCUMULATION TIME 300 s, ACCUMULATION POTENTIAL –240 mV, n = 5)

x_i (μM) taken	$\overline{X}$ (μM) found	SD (μM)	$\frac{SD}{\sqrt{n}}$ (μM)	$\overline{X} \pm \frac{t \cdot SD}{\sqrt{n}}$ (μM)	RSD (%)
0.050	0.048	0.002	0.001	0.048 ± 0.003	4.5
0.100	0.101	0.004	0.002	0.101 ± 0.005	4.2
0.200	0.200	0.008	0.004	0.200 ± 0.010	4.0
0.300	0.302	0.011	0.012	0.302 ± 0.032	3.8
0.400	0.398	0.014	0.014	0.398 ± 0.039	3.5
0.500	0.503	0.016	0.017	0.503 ± 0.046	3.3
0.600	0.598	0.019	0.019	0.598 ± 0.053	3.2
0.800	0.796	0.025	0.020	0.796 ± 0.055	3.1
1.000	1.000	0.030	0.013	1.00 ± 0.037	3.0
2.000	1.970	0.055	0.055	1.97 ± 0.153	2.8
3.000	2.980	0.080	0.081	2.98 ± 0.223	2.7
4.000	4.020	0.100	0.101	4.02 ± 0279	2.5
5.000	5.040	0.121	0.121	5.04 ± 0.336	2.4
6.000	6.000	0.144	0.144	6.00 ±0.340	2.4
8.000	8.000	0.200	0.200	8.00 ± 0.555	2.5
10.000	9.950	0.288	0.289	9.95 ± 0.801	2.9

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