Asian Journal of Chemistry Vol. 22, No. 6 (2010), 4611-4616

Determination of Selenium in Thioridazine Hydrochloride by Differential Pulse Anodic Stripping Voltammetry

ZOHREH MODARES TEHRANI*, ZOHREH FARAHANI, AFSHIN MOHAJER and JAMSHID MOFIDI†
Department of Chemistry, Alzahra University, Tehran, Iran
E-mail: zmodares@yahoo.com

In present studies, the ability of anodic stripping voltammetry (ASV) on hanging mercury drop electrode (HMDE) has been investigated by studying the different influencing parameters. The proposed method, based on anodic stripping voltammetry of CuSe(Hg) at hanging mercury drop electrode provides a simple and sensitive approach for determination of selenium in thioridazine hydrochloride. Under optimized conditions, detection limit was 0.2 μg/L and repeatability of the method expressed by relative standard deviation (RSD) for selenium was 2.5 % at 30 μg/L and 9.2 % at 0.5 μg/L and also, the calibration curve was linear over the range of 0.2-30.0 μg/L (R^2 = 0.9966, P < 0.0001).

Key Words: Selenium, Thioridazine hydrochloride, Stripping voltammetry.

INTRODUCTION

Selenium, a non-metallic element, accompanies sulfur as an impurity in the synthesis of thioridazine hydrochloride which is an antipsychotic drug[1,2]. Because of selenium toxicity at low content, it is necessary to use a precise and reliable analytical method for determination of this element. In the United Stated Pharmacopoeia (USP) 28, the recommended method is oxygen flask combustion and determining a selenium complex absorbance in visible region. The sample digestion method is dangerous, tedious, time consuming and accompanies by experimental errors. Therefore, it is necessary to develop a simple and reliable analytical method[3]. The high sensitivity of neutron activation method has made it appealing, but the special skills, time and cost essential are required for this technique[4,5]. A few studies have employed atomic absorption, ultraviolet or fluorometric spectrophotometry. But, these techniques often require prior chemical separation of selenium in order to eliminate interferences in the analysis[6,7]. Electrochemical techniques, especially differential pulse anodic stripping voltammetry (DPASV) provides a simple, highly sensitive and relatively inexpensive approach for determining selenium in most matrices[4,8]. Many researchers reported interference of copper with selenium peak height in voltammetric methods[9] and we took advantage of this phenomenon in determination of selenium. Then, in this study, the influence of various parameters

†Islamic Azad University, North Tehran Branch, Tehran, Iran.

such as potential deposition, deposition time and pH were investigated on selenium peaks in differential pulse anodic stripping voltammetry method.

EXPERIMENTAL

Voltammograms were prepared by using of a trace analyzer model No. 746 (Metrohm AG Ltd., Switzerland). The cell was a three-electrode system consisting an Ag/AgCl electrode, a hanging mercury drop electrode and a platinum electrode as reference, working and auxiliary, respectively. All the reagents including selenium dioxide, acetic acid, sodium acetate, copper nitrate, sodium chloride, hydrochloric acid, perhydrol 30 % and nitric acid were analytical grade from Merck.

Method: A 100 mg sample of thioridazine hydrochloride was acurately weighed into a flask. Then 6 mL of nitric acid and 1 mL of oxygen peroxide were added to the flask and heated on the hot plate until the volume was decreased to 2-3 mL. The flask was removed from the hot plate and allowed to cool to room temperature. Then 0.5 mL of HCl was added and heated on the hot plate until a brown gas appeared. After removal of the gas, the flask was allowed to cool. The solution was transferred into a 100 mL volumetric flask and then diluted to volume with double distilled water. The sample was analyzed by the mentioned optimized method. At first, 10 mL of buffer was pipetted into the volumetric cell and then added, 1 mL of the Cu^{2+} solution (100 mg/L), 0.1 mL of the sample solution. The solution was deoxygenated for 300 s by high purity argon, while stirring the solution. A fresh mercury drop was extruded as working electrode. Then stirring and electrolysis were carried out for 30 s at -350 mV. The stirrer was stopped for 10 s, the potential was scanned from -350 to +800 mV with a rate of 60 mVs and a pulse height of 100 mV.

Buffer solution was prepared by mixing different parts of sodium acetate-sodium chloride (0.2 M) and acetic acid-hydrochloric acid (0.2 M). An aliquot of 10 mL of the buffer solution (0.2 M) was adjusted to desired pH and then added to the voltammetric cell, 1 mL of Cu^{2+} solution and 0.1 mL of the selenium solution.

RESULTS AND DISCUSSION

Several experiments were performed in differential pulse mode using the buffer as a supporting electrolyte.

Effect of Cu^{2+} concentration: Anodic stripping voltammetry of Se(IV) without addition of Cu^{2+} produced a peak at -540 mV due to formation of the selenium during the deposition step[4,8,10,11]:

$$H_2SeO_3 + 4H^+ + Hg + 4e^- \rightarrow Se(Hg) + 3H_2O \quad (1)$$

In the presence of Cu^{2+}, a new peak appeared in a more positive potential because of formation an intermetallic compound[4,10].

$$H_2SeO_3 + 4H^+ + Cu^{2+} + Hg + 6e^- \rightarrow CuSe(Hg) + 3H_2O \quad (2)$$

The peak potential varied with Cu^{2+} concentration and shifted in a negative direction as Cu^{2+} concentration increased up to 100 mg/L (Fig. 1). These changes

were perhaps due to the formation of stable intermetallic compound on the electrode surface[11]. We also have studied the effect of copper concentration on the peak current (Fig. 2). A concentration of 100 mg/L was found to be optimum for analytical purposes.

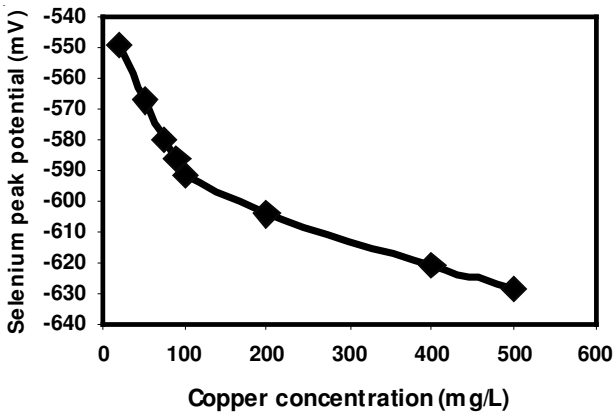

Fig. 1. Effect of copper concentration on the peak potential. Se concentration, 3 ppb; operating mode, DPASV; working electrode, HMDE; supporting electrolyte, sodium acetate-acetic acid and sodium chloride-hydrochloric acid buffer (0.2 M); pH, 1; deposition time, 30 s; deposition potential, -350 mV; pulse height, 100 mV

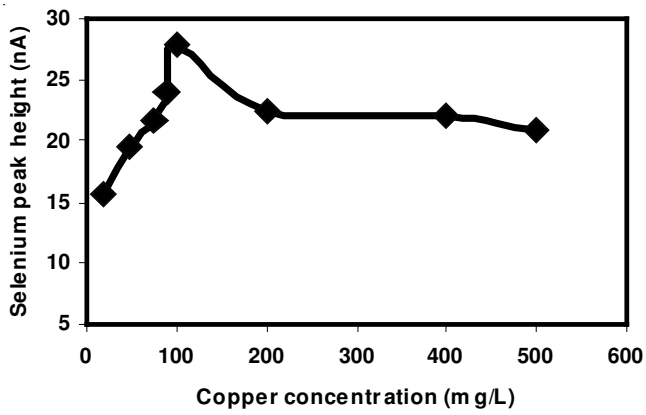

Fig. 2. Effect of copper concentration on the peak current. (Same condition as Fig. 1)

Effect of pH: The supporting electrolyte was acetic acid-sodium acetate and hydrochloric acid-sodium chloride buffer (0.2 M). The peak potential shifted in a positive direction by decreasing the pH from 5-1 (Fig. 3). The peak height increased by lowering pH (Fig. 4) and at higher pH, the sensitivity of the determination was decreased. Thus, a pH = 1 was suitable for the determination of selenium under the optimized conditions.

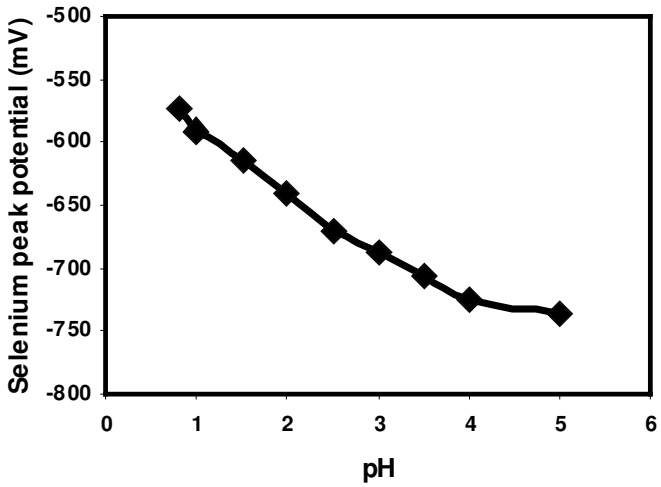

Fig. 3. Effect of pH on the selenium peak potential. Se concentration, 3 ppb; operating mode, DPASV; working electrode, HMDE; supporting electrolyte, sodium acetate-acetic acid and sodium chloride-hydrochloric acid buffer (0.2 M); copper concentration, 100 mg/L; deposition time, 30 s; deposition potential, -350 mV; pulse height, 100 mV

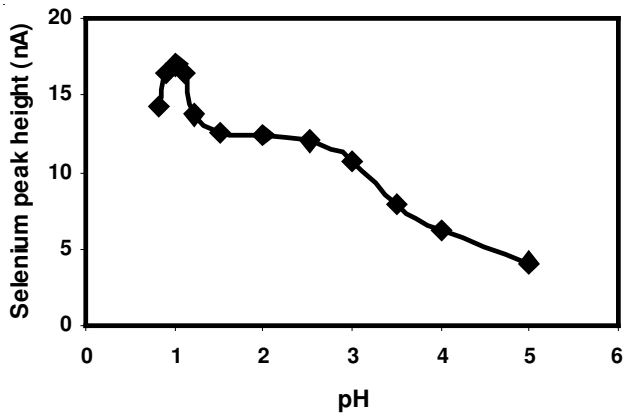

Fig. 4. Effect of pH on the selenium peak current (Same condition as Fig. 3)

Effect of the deposition potential: In the stripping procedure, accurate determination of the elements in acidic media is based on the use of deposition potential. In order to obtain a well defined reduction or oxidation peak, the optimum deposition potential must be obtained[12]. Then, the DPASV procedure was carried out on the HMDE for 30 s at several selected potentials between -200 to -500 mV. The relationship between the peak current of selenium and deposition potential is shown in Fig. 5. Selenium could be deposited efficiently on the electrode at -350 mV. In practice, the deposition potential was fixed at -350 mV.

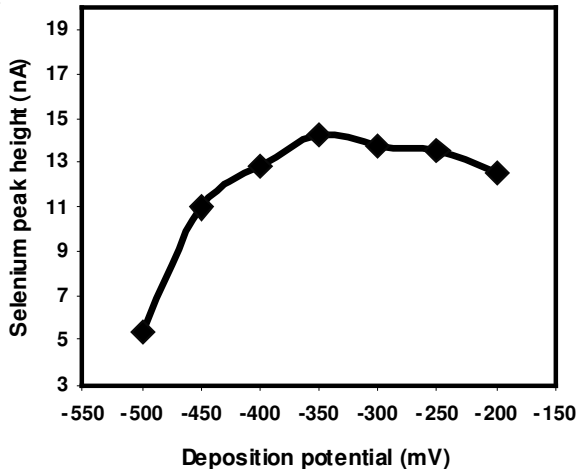

Fig. 5. Effect of deposition potential on the selenium peak current. Se concentration, 3 ppb; operating mode, DPCSV; working electrode, HMDE; supporting electrolyte, sodium acetate-acetic acid and sodium chloride-hydrochloric acid buffer (0.2 M); pH, 1; copper concentration, 100 mg/L; deposition time, 30 s; pulse height, 100 mV

Effect of deposition time: The peak current for selenium in the thioridazine hydrochloride sample was measured using DPASV as a function of deposition time in order to optimize analytical procedure. It was found that selenium peak current increased with increasing deposition time less than 30 s and it was nearly constant at more than 30 s (Fig. 6).

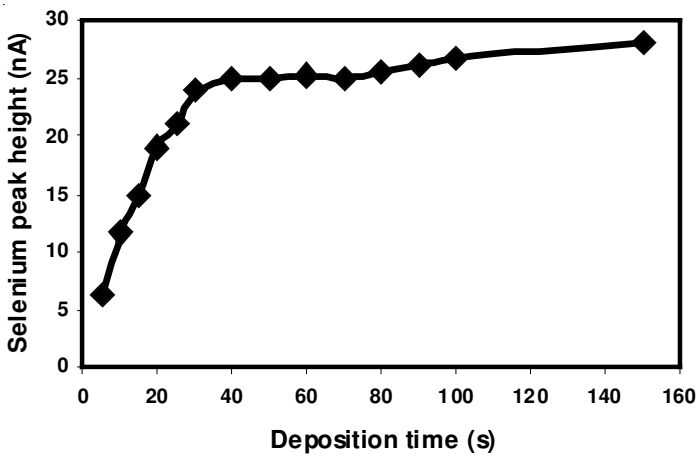

Fig. 6. Effect of deposition time on the selenium peak current. Se concentration, 3 ppb; operating mode, DPASV; electrode, HMDE; supporting electrolyte, sodium acetate-acetic acid and sodium chloride-hydrochloric acid buffer (0.2 M); pH, 1; copper concentration, 100 mg/L; deposition potential, -350 mV; pulse height, 100 mV

The precision and validation data are presented in Table-1. Present investigations demonstrate, that the proposed method based on DPASV has other advantages including low cost apparatus and instrumentation.

TABLE-1
RECOVERY, PRECISION (RSD %), SENSITIVITY, LINEARITY RANGE AND LIMITS OF THE METHOD

Recovery			
Sample (n = 5) (mg/Kg)	Spike added (mg/Kg)	The spike added sample (n = 5) (mg/Kg)	Recovery (%)
1151.2 + 47.8	100	1249.6 + 27.7	99.0
	500	1647.6 + 54.4	99.3
	1000	2150.3 + 83.9	99.9
Precision (RSD %)			
	Repeatability (n = 10) (%)	Internal reproducibility (n = 5) (%)	
Sample (1136.6 mg/Kg)	2.0	2.5	
Standard (0.5 µg/L)	9.2	13.1	
Standard (5.0 µg/L)	4.3	10.3	
Standard (15.0 µg/L)	2.7	6.1	
Standard (30.0 µg/L)	2.5	5.5	
Sensitivity and Linearity range			
Calibration range (n = 3)	r^2	Slope [nA/(µg/L)]	Intercept (nA)
0 - 30.0 µg/L	0.9966	2.2504	7.7624
Limits			
Detection limit 0.2 µg/L		Quantitation limit 0.6 µg/L	

ACKNOWLEDGEMENTS

The authors acknowledge support of Sarmad-Teb Co. Ltd. (Metrohm distributor in Iran) and would like to thank Minoo Pharmaceutical Co. for supplying pure drug compound.

REFERENCES

1. Merck Index, Merck and Co. Inc., edn. 30, Vol. 2, p. 8505 (2001).
2. Martindale, Pharmaceutical, edn. 33, Vol. 708, p. 1 (2002).
3. United States Pharmacopoeia (USP) 28, Official Monographs, Thioridazine Hydrochloride and <291> 2303, <471> 2333.
4. S.B. Adeloju, A.M. Bond, M.H. Brigges and H.C. Hughes, *Anal. Chem*., **55**, 2076 (1983).
5. K. Jorstad and B. Salbu, *Anal. Chem*., **52**, 672 (1980).
6. Ph. Breyer and B.P. Gilbert, *Anal. Chem. Acta*, **201**, 23 (1987).
7. B.L. Dennis, J.L. Moyers and G.S. Wilson, *Anal. Chem*., **48**, 1611 (1976).
8. R.W. Andrews and D.C. Johnson, *Anal. Chem*., **47**, 294 (1975).
9. H. Aydin and G.H. Tan, *Analyst*, **116**, 941 (1991).
10. V. Stara and M. Kopanica, *Anal. Chem. Acta*, **208**, 231 (1988).
11. C.M.G. van den Berg and S.H. Khan, *Anal. Chem. Acta*, **231**, 221 (1990).
12. R. Inam and G. Somer, *Food Chem*., **66**, 381 (1999).

(*Received*: 14 September 2009; *Accepted*: 17 February 2010) AJC-8450