Research Journal of Recent Sciences ISSN 2277-2502
Vol. **2(ISC-2012),** 51-54 **(2013)** *Res. J. Recent. Sci.*

A Simple Method for Voltammetric Determination of Trace Amounts of Selenium in Diverse Matrices

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Available online at: www.isca.in
Received 31th July 2012, revised 18th December 2012, accepted 17th January 2013

Abstract

A simple and convenient method is described for the determination of low concentration selenium in samples of industrial waste and vitamin tablet. The method is based on the differential pulse polarographic reduction of Se (IV) in presence of alanine in ammonium chloride medium. Linearity of the calibration curve was achieved upto 44ppm with a limit of determination of 5 μg/L. Major metal ions copper, lead and zinc did not interfere.

Keywords: Selenium, differential pulse polarography, industrial wastes, vitamin tablet.

Introduction

The semiconductor properties of selenium has made it immensely important element. Selenium and its compounds have thus found applications in photochemical cells, photocopiers, solar cells and as a catalyst. Selenium is also essential to some species including humans. Se acts to stimulate the metabolism. In regard to toxicity, selenium compounds are very hazardous by inhalation and intravenous routes[1]. The microorganisms in water sediments and sewage can convert inorganic forms of selenium to toxic organic products like dimethyl selenide, $(CH_3)_2Se$ [2]. Therefore, it is appropriate to develop a simple analytical method for the determination of trace selenium.

Selenium is considered to be present with three oxidation states of +6, +4 and -2. Voltammetric methods such as anodic stripping voltammetry and differential pulse polarography (DPP) can identify and determine different ionic forms of an element due to the certain selectivity of the redox potential[3]. These methods are thus more suitable for the studies and determination of selenium. In stripping analysis intermetallic compound formation on the electrode surface causes significant interference during the deposition[4], therefore, we have envisaged the suitability of DPP in present work. The observations have enabled in developing of the optimal conditions for the determination of selenium at low concentration. DPP determination of arsenic[5], germanium[6], tellurium[7] and gallium[8] were reported earlier.

Method and Materials

Instrumentation: A microprocessor based pulse polarographic analyzer (Model CL–362) in combination with a drop–timer assembly, all of Elico Limited, Hyderabad, India, was used for voltammetric measurements. Voltammograms were recorded by an Epson printer (Epson-LX-300+II).The instrumental settings for DPP were as follows: a DME was used as working electrode; pulse amplitude, 50 mV; drop time, 0.5 s; scan rate, 12 mV/s, and charging current compensation, 20%. Potentials were measured against a saturated calomel electrode (SCE). A platinum wire was used as an auxiliary electrode.

An atomic absorption spectrophotometer (Model – AA 2380, Perkin Elmer) USA, was also used for sample analysis. The instrument has a Czerny tuner grating monochromator with a wavelength range of 1900-9000A^0. Slit-Width is selectable in three modes of 1.9, 3.8 and 9.5A^0.Sample aspiration flow control is adjustable by variable 3-line flow system.

Sample Preparation: The real samples of industrial waste and vitamin tablet were prepared for analysis of selenium in view of wide industrial and pharmaceutical uses of selenium and selenium compounds in different forms.

Industrial waste water samples were collected in cleaned polyethylene containers from different industries located in Basni Industrial Area of Jodhpur. Glasswares were soaked in 2 M nitric acid for atleast one week and washed several times prior to use to avoid contamination. Collected samples were filtered in order to separate any suspended particulate matter and acidified with HCl to pH~2 for storage[9].

Sample treatment: A 50 ml aliquot of sample was treated with 1ml of oxidizing mixture of nitric acid and sulphuric acid to destroy the biological and organic matters. The contents were heated on a hot plate until the solution fumed and then were transferred to a volumetric flask with requsite volume of distilled water[10].

The vitamin tablet containing selenium was powdered and dissolved in doubly distilled water to prepare test solution for DPP determination. It was filtered and made up to the requisite volume[11].

Test solutions were deaerated for 20 min. by passing nitrogen. It was purified by bubbling through a vanadous chloride scrubbing solution[12]. Chemicals used were of analytical grade. Stock solution of selenium was prepared from selenium dioxide of Loba Chemie. All experiments were carried at ± 298K.

Results and Discussion

Electrochemical characteristics: The electrochemical data on selenium has indicated that the standard reduction potential of Se^{4+} (+0.74V) is very near to that of Hg^{2+} (+0.79V)[13]. Therefore, it is rather difficult to study selenium in simple electrolytes. However in presence of a complexing medium electroreduction of Se (IV) is reported[14]. In this way the authors have utilized the complexing ability of alanine to investigate Se (IV) / Se (0) system. The supporting electrolyte used was 0.01 M ammonium chloride.

Preliminary observations showed that selenium (IV) gave a well-defined polarographic wave for its reduction to selenium (0) at -1.73V. The wave height was found optimum at a concentration of 0.01M alanine in 0.01M NH_4Cl. The wave appeared to be diffusion controlled and electrode process was not found fully reversible[15].

Optimum DPP Conditions: DPP reduction of selenium (IV) gave a sharp DP peak at -1.73V. Linearity of peak current versus concentration was noticed in range of 0.005 to 40 ppm. The calibration curve is drawn in figure-1 and its characteristics are given in table-1.

Table-1
Characteristics of calibration curve of Selenium (IV)

Slope	0.068
Intercept	0.094
Coefficient of correlation (r)	0.999

Accuracy and precision: A test solution (2 µg/ml Se (IV)) was analyzed under the optimized experimental conditions to evaluate the reproducibility of the DPP measurements. The results obtained were in good agreement with a relative error of 1.52%, inferring that DPP determination of selenium is precise and accurate.

Interference study: The peak potential of Se (IV) in presence of alanine in 0.01M NH_4Cl medium was noted at -1.73V. This makes it very convenient to determine selenium in presence of other metal ions such as lead, cadmium and zinc, commonly present in industrial wastes[16]. Copper, in particular, might be associated with selenium as latter is obtained in the form of a byproduct of Cu refining. The DP peak of Cu (II) occurred at -0.11V. Similarly, peak potential of Pb (II) and Cd (II) were found well-separated at -0.38V and -0.55V, respectively. Zn (II) also showed a distinguishable DP peak at -1.04V. Thus, these metal ions did not interferred. It has been further clarified in figure-2.

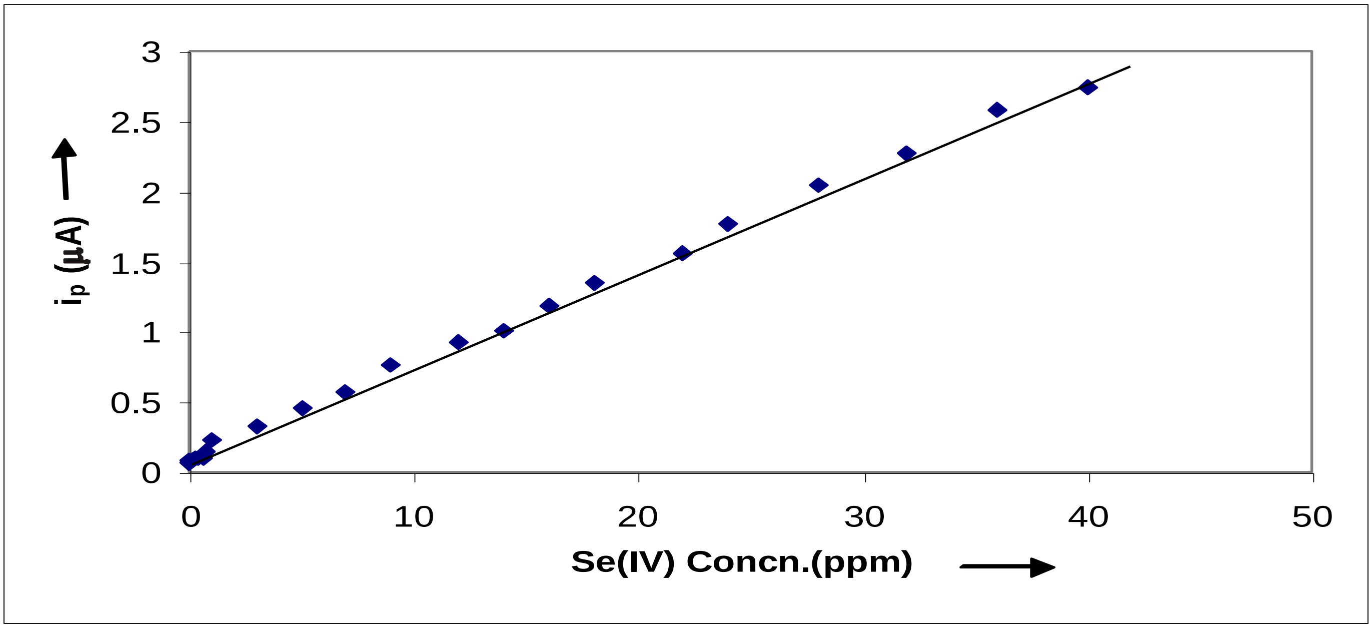

Figure-1
Calibrations curve of selenium (IV), concentration vs peak current, in 0.01M alanine− 0.01M NH_4Cl

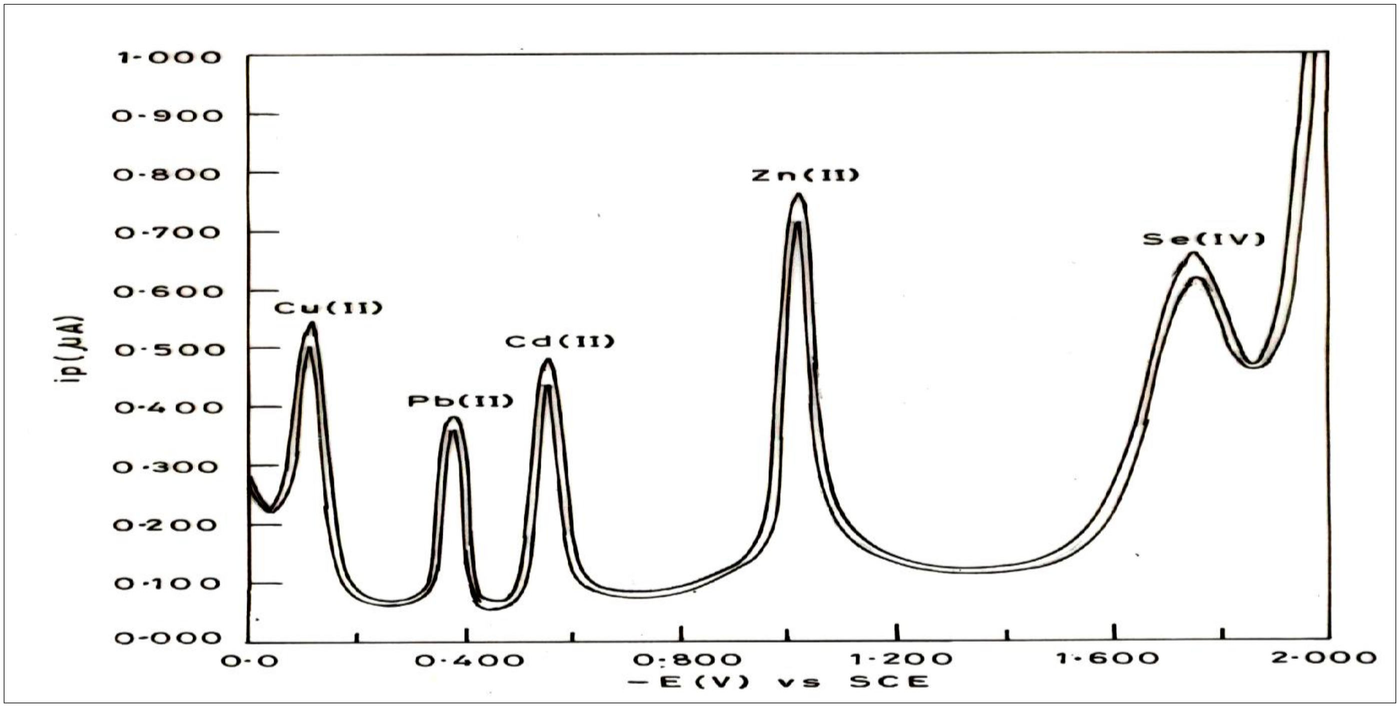

Figure-2
DP polarogram of selenium (IV) in presence of copper, lead, cadmium and zinc in 0.01M alanine − 0.01M NH_4Cl., Cu (II),8ppm; Pb (II),20ppm; Cd (II),8ppm; Zn (II),0.6ppm and Se (IV),6ppm, Modulation amplitude, 50 mV; pulse duration, 57ms; drop time, 0.5 s and scan rate 12 mV/s

Limit of determination: The detection limit of selenium was achieved to be 5µg/L using DPP.

Analytical Applications: The optimum DPP conditions in terms of polarographic medium, calibration linearity, reproducibility and detection limit were applied to analyse selenium in different samples of industrial waste and vitamin tablet.

A measured volume of the prepared sample was taken into the polarographic medium of 0.01M alanine in 0.01M NH_4Cl. Polarograms were recorded from -1.2 to -2.0 V and peak current was measured at -1.73 V after making the blank correction. Standard addition method was used to determine concentration of selenium in samples[17]. The results of determination of selenium in industrial wastes and vitamin tablet are summarized in table-2.

Table-2
DPP determination of selenium in different samples

S. No.	**Sample**	**Se concentration (ppm)**	
		DPP ± SD	**CV (%)**
1.	**Industrial Waste**		
	Mehta Industry	0.729 ± 0.003	0.37
	J.P.Industries	0.432 ± 0.003	0.65
2	**Vitamin tablet** (1.0)$	0.769 ± 0.011	1.49

No. of determinations =5, $ From Banner –Glaxo Smith Kline Pharmaceuticals, Value shown in parenthesis is cited value of Se in tablet

The determination of selenium by DPP was found more suitable to stripping voltammetry because of higher negative reduction potential of Se (IV) at -1.73V. Otherwise other interfering metal ions like Cu (II), Pb (II) and Zn (II) would also been deposited on the surface of electrode and making inconvenient voltammetric measurements. Herein it was also observed that limit of determination could be lowered down from 50µg/ml to 5µg/ml in presence of selective complexing reagent by using DPP[18].

Conclusion

DPP measurements of selenium in different samples were further verified by carrying out the comparative studies with AAS method. The data are shown in table-3. The results of selenium determination are also in good agreement with other techniques including DPP reported by Nagaosa and Ono[19]. High sensitivity of the employed method must further be accompanied by sufficient selectivity, precision and accuracy. In this way several methods such as spectrophotometry[20,21], AAS[22,23], and XRD[24] are reported in determination of microgram level of various metal ions. Even compared to anodic stripping voltammetric determination of selenium in terms of detection limit (4µg/L)[25] the suggested DPP method is quite reasonable.

Table-3
Comparison of results of determination of selenium by DPP and AAS

Sample	**Se Concn. (ppm)**	
	DPP	**AAS ± SD**
1.	0.729	0.728
2.	0.432	0.431
3.	0.769	0.770

Sample 1and 2 from Mehta and J.P. Industry, Sample 3 Vitamin tablet

Acknowledgement

The authors acknowledge financial support to V. Kherwa under ‘UGC Research Fellowship in Science for Meritorious Students’ (RFSMS).

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