Trace Determination of Selenium by DPP and DPCSV

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Trace level analysis of seleniuum is of great importance owing to its toxic nature and carcinogenicity. The metaloid can induce a fatal syndrome known as 'Selenosis' in animals when its uptake exceeds a particular limit. On the other hand, its deficiency is known to cause muscular dystrophy. Various voltammetric procedures such as square wave polarography [1], differential pulse polarography [2], differencial anodic and cathodic stripping voltammetry [3,4] have been employed for the determination of selenium. Present paper describes differential pulse polarography (DPP) as well as differential pulse cathodic stripping voltammetry (DPCSV) procedures for trace determination of Se(IV). The developed methods have been extended to the determination of selenium in plant material, in skimmed milk powder and in semiconductor material. It has also been possible to carry out simultaneous determination of selenium and tellurium.

EXPERIMENTAL

Investigations were carried out on Metrohm Polarecord E-506 with attached polarography stand (E-505). The electrode system consisted of dropping mercury electrode (DME) or hanging mercury drop electrode (HMDE) as the working electrode. Ag/AgCl/satd. KCl electrode was the reference and platinum metal was the auxiliary electrode. All chemicals used were of AR grade and triply distilled water was used for preparation of stock solutions. Selenium solution was prepared by dissolving a known weight of SeO_2 (AR, E.Merck) in water. It was suitably acidified. Working solution of Se(IV) (25 g/25 l) was obtained by suitable dilution.

DPP Determination of Se(IV)

Optimum recording conditions were found to be as follows: Voltage scan range -0.2 V to -1.2 V, scan rate 8 mV/sec, paper speed 120 mm/min, drop time 1 sec and pulse amplitude 12 mV. Reduction of Se(IV) at DME in various acid media (H_3PO_4, $HClO_4$, HCl, HNO_3 and H_2SO_4 - 0.2, 0.1, 0.05 and 0.01 M) were investigated. Studies were carried out in acetate buffer at pH 4.5, 4.7, 5.0, 5.2 and 5.5. Se(IV) gave a well defined, sharp peak in all these media. Waves shifted cathodically and I_p increased with decrease in acid concentration. 0.01 M HCl was chosen as it gave maximum peak current with high reproducibility. Addition of TX-100 (0.2×10^{-4} %) showed improved peak symmetry and was used as a maximum supressor.

The following procedure was followed in analysis: In a polarography cell, 25 ml of 0.01 M HCl and 50 µl of 0.01 % TX-100 were taken and nitrogen was bubbled for 15 minutes. A blank was recorded. Selenium solution (3 ppm) was added and polarogram was recorded. A peak was obtained at -0.584 V with I_p of about 800 nA.

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Calibration plots were linear in the range 10 ppm to 2 ppb. The lowest determinable limit was 20 ppb with RMD of 1.2% SD and CV values were 0.05 and 1.6% respectively. Amongst various ions studied, Ni^{2+} could be tolerated upto 100 times, Zn^{2+} could be tolerated upto 20 times and five fold excess of Sn^{2+} and Tl^{+} could be tolerated. Pb^{2+}, Sb^{3+}, Bi^{3+} and Cu^{2+} interfered. Analysis of Se(IV) in spiked water samples was carried out. The average percent recovery was found to be 98% in 0.2 ppm solution and 96% in 0.5 ppm solution.

DPCSV Determination of Se(IV)

Se(IV) has been determined by DPCSV. Recording conditions employed were as follows: deposition potential -0.4 V; scan range -0.4 V to -2.4 V; scan rate 10 mV/ sec; pulse amplitude 40 mV and paper speed 75 mm/min.

Out of various electrolytes studied for selenium, results obtained with $HClO_4$ (0.1 and 0.01 M), CH_3COOH (1 and 0.1 M) and H_3PO_4 (0.4, 0.1 and 0.01 M) were satisfactory. Other electrolytes investigated were HNO_3 (0.5 and 0.1 M), $NaNO_3$ (1 and 0.5 M), TEA (1 M), valin (1 M), NaCl + NaOH (0.1 M each) and NH_4Cl + NH_4OH (0.5 M + 0.1 M and 0.1 M + 0.1 M). A sharp cathodic dissolution peak with appreciable peak current was observed in acid media. The E_p values tend to shift towards cathodic potentials with decrease in acid concentration. 0.01 M $HClO_4$ was found to be more suitable for selenium as it gave well resolved, sharp peak with smooth base line.

The following procedure was used for analysis: To a cell containing 25 ml of 0.01 M $HClO_4$ were added 25 µl of Se(IV) solution (10 ppb) and deaerated for 15 minutes. The polarogram was recorded under optimum conditions (specified above). A sharp peak was obtained at -0.592 V with I_p of 150 nA. Effect of electrode dimension and enrichment time on Se(IV) peak was studied. Electrode surface area of 1.82 mm^2 and pre-electrolysis time of 60 sec with quiescent period of 10 sec was chosen in studies.

Current - concentration relationship was found to be linear over the range of 0.2 ppb to 100 ppb of Se(IV). Minimum determinable limit was 0.2 ppb with relative mean deviation of 4.6%. SD and CV values were 0.08 and 7.9% respectively. Various cations were studied for their possible interference. Te(IV) and V(V) could be tolerated upto 10 times and 8 times respectively. As(III) upto 6 times, thalous upto 5 times and Zn^{2+}, Mn^{2+} and Sn^{2+} were tolerated upto 4 times. Sb^{3+}, Bi^{3+}, Ni^{2+} and Mo(VI) could be tolerated upto 2 times whereas Cu^{2}+ was tolerated only in 1:1 ratio.

The cathodic dissolution reaction taking place at HMDE is attributed [5,6] possibly to

$$Se^{4+} \xrightarrow{(1)} Se^{0} \xrightarrow{(2)} Se^{2-}$$

Determination of Selenium in Plant Materials and Skimmed Milk Powder

3 g wheat flour sample was accurately weighed and transferred to a beaker, 20 ml HNO_3 were added, beaker was covered

with a watch glass and the contents were digested by heating gently. The solution was heated till dryness. This process was repeated twice. The residue was dissolved in twice distilled water and volume was made upto 50 ml. 5 and 10 ml aliquots were analysed. Selenium content was calculated by calibration curve as well as standard addition method, using DPCSV technique.

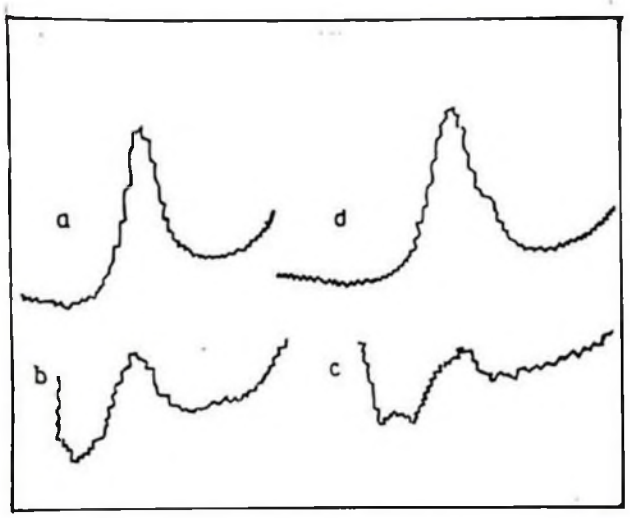


Fig.1: Determination of Se(IV) in plant materials and semiconductor.

Ep = 0.526 V : 1 cm = 3.75 nA.
a) Wheat flour :
b) Skimmed milk powder
c) Dry Cabage leaves
d) Semi conductor

Skimmed milk powder and dried and powdered cabbage leaves were processed exactly in a similar manner as described above (Fig. 1 a,b,c).

Determination of selenium in semiconductor material

The semiconductor plate was cut into pieces and 0.4 g were treated with HNO_3 + HCl (20 ml, 1:3). The solution was boiled till drynesss. 15 ml water was added and was again heated till dryness. The residue was taken up in water and volume was made upto 50 ml. This solution was further diluted 400 times. 1 and 2 ml aliquots were analysed. Results obtained by calibration curve and standard addition method were in full agreement with each other (Fig. 1,d).

Simultaneous determination of Se(IV) and Te(IV)

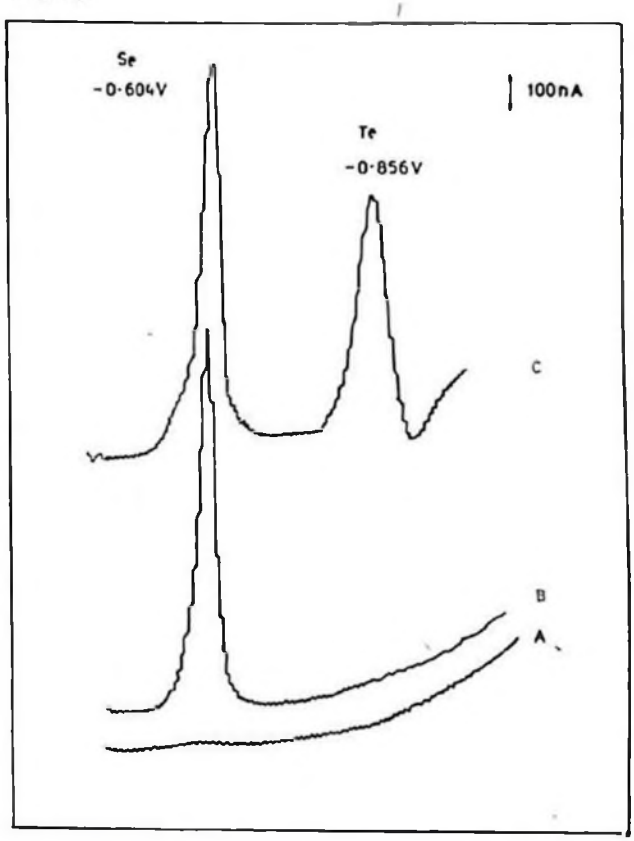


Fig. 2: Simultaneous Determination of Se(IV) and Te(IV)

A - Blank
B - 60 PPb Se
C - 60 PPb Se + 10 PPb Te

Se(IV) and Te(IV) gave sharp and well separated signals at -0.604 V and -0.856 V respectively. A synthetic mixture containing these two ions was prepared and voltammogram was recorded (Fig.2). Recovery of each ion was computed by standard addition method. Results obtained were satisfactory. The procedures developed by us are accurate and precise as is evident from standard deviation and co-efficient of variation data and could be used successfully in routine analysis.

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