Differential pulse polarographic trace level determination of selenium

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The electrochemical behaviour of selenium(IV) has been studied employing DC polarography, cyclic voltammetry and differential pulse polarography. Optimum conditions for trace level determination of selenium in presence of cadmium, lead, copper and zinc have been determined. A detection limit of 50 μg/L is achieved. The method has been successfully applied for the determination of selenium in water samples of industrial waste, ground/well, ponds, lakes and river.

The determination of toxic trace metals in industrial waste waters has gained wide attention as seepage of effluents cause metal pollution of the aquatic environment. In view of wide applications of selenium in industries and its detrimental effects, it is important to determine selenium concentrations in different aquatic systems. In the present note, a differential pulse polarographic (DPP) method has been proposed for the determination of selenium in ammonia-ammonium chloride buffer medium. The method is used to determine selenium contents in water samples of industrial wastes, ground/well, ponds/lakes and river.

Experimental

A polarographic analyzer (Model 174-A) in conjunction with a drop timer (Model 174/70) and X-Y recorder (Model RE-0074, Princeton Applied Research Corporation, EG&G, U.S.A.) were used for DC and DPP experiments. The instrumental settings for DPP were as follows: a dropping mercury electrode was used as the working electrode, modulation amplitude 50 mV, pulse duration 57 ms, clock time of pulse 1s, and scan rate 5 mV/s. Potentials were measured against a saturated calomel electrode (SCE). Cyclic voltammetry was performed on a cyclic voltammmograph (Model CV-27) of Bioanalytical systems, U.S.A. in which a hanging mercury drop electrode (HMDE) and Ag/AgCl were used as working and reference electrodes respectively. The scan rate varied from 20 to 100 mV/s. A platinum wire was used as an auxiliary electrode in all observations.

Samples were collected from Marudhar and Basni industrial areas near Jodhpur, having industries of dye production, non ferrous metal, smelting, paint and pigments, and chemicals. All glasswares and polyethylene sample containers were soaked in 2 M HNO₃ for at least one week and washed several times with doubly distilled water. Water samples were filtered to remove suspended particulate matter and were preconcentrated to one tenth of their original volume by evaporation to obtain detectable quantities of selenium. To 100 ml of this aliquot, 1 ml of an oxidising mixture of nitric acid, sulphuric acid and perchloric acid was added, the contents were heated until the solution fumed to destroy biological and organic matter. Contents were transferred to a volumetric flask and made up to the requisite volume. Natural water samples of ground, lakes and river were also treated in the same manner.

All the experiments were carried out at 25 ± 1°C. The solutions were deaerated by bubbling purified nitrogen for 20 min prior to voltammetric measurements. Nitrogen was purified by passing it through a vanadous chloride solution. All chemicals used were of reagent grade purity. Solutions were prepared in doubly distilled water.

Results and discussion

Preliminary observations on electroreduction of Se(IV) indicated suitability of NH₃-NH₄Cl buffer among various supporting electrolytes studied, viz., KCl, HCl, HClO₄, acetate buffer and phosphate buffer. All measurements were therefore made in this buffer where a well defined polarographic wave of Se(IV) to -2 state was observed at -1.68 V. The half wave potential (E½) of the wave was found to be pH dependent. At higher pH (10.0) the wave shifted to more negative potentials and merged with final current rise while at pH 8.5, the wave appeared to be diffusion-controlled. The nature of the electrode reaction was investigated by performing cyclic voltammetry at HMDE in the potential range of -1.2 to -1.8 V where it showed a lone cathodic peak (Epc = -1.60 V vs Ag/AgCl) at the scan rate 60 mV/s with no corresponding anodic peak, illustrating the irre-
VERSIBLE process (Fig. 1) under these experimental conditions.

Se(IV) also showed sharp DP peak at -1.67 V. A linearity between peak height and Se(IV) concentration was observed between 0.05 and 8.13 ppm. The characteristics of the calibration curve were as follows: slope = 1.09 ± 0.008; coefficient of correlation ($r$) = 0.9996 and standard deviation, $sd$ = 0.089.

The DP peak was found suitable for quantitation of selenium where a limit of determination was achieved (50 µg/L).

Interference

DP polarograms of selenium were also recorded in presence of other common cations such as Cu$^{2+}$, Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ (1 mg/L). The DP peaks of these metal ions were distinguishable from each other and indicated no interference in the determination of selenium as shown in Fig. 2. The interference of coexisting metal ions (Ni$^{2+}$, Co$^{2+}$, Cr$^{6+}$) in industrial effluents was also checked at low concentrations.

Determination of selenium

DPP reduction of Se(IV) in ammoniacal media was made the basis of selenium determination in aqueous systems. The recovery and the selectivity of the method were estimated by determining selenium in synthetic samples. DP polarograms were recorded in the potential range of -1.4 to -1.8 V and currents were measured at -1.68 V after making blank corrections. Concentration of selenium was determined by standard addition method. The observations are summarised in Table 1. Prepared industrial waste water and other water samples were analysed for selenium contents in this manner. The selenium concentrations in industrial waste waters and river were found within the limits of 24.0 - 91.0 (Ar 54.1) µg/L and 20.0 - 62.2 (Ar 30.6) µg/L, respectively. The presence of selenium in industrial waste waters may be due to the use of selenium and its compounds in industries of dye production, non-ferrous metals, smelting, paint and pigments, and chemicals. Selenium could not be detected in water samples of ground/well and ponds/lakes which may be due to the presence of selenium at ultra trace (sub micro) levels in these samples.

The peak potential of Se(IV) in NH$_3$-NH$_4$Cl buffer occurred at more negative potential, i.e., -1.67 V, thus, it was convenient for measurements when Se was present along with copper, lead, cadmium and zinc at lower concentrations.

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References


