Enhancement of the Sensitivity of Tungsten Determination by Catalytic Current Polarography

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A new method based on catalytic current in differential pulse polarogrms in a medium containing chlorate and 8-hydroxyquinoline (oxine) is described for the determination of tungsten. Experimental conditions such as pH and the composition of supporting electrolyte are optimized to get a linear calibration graph and also to lower the detection limit. The influence of possible interferences on the catalytic current has been investigated. The mechanism of the electrode process is studied using DPP diagnostic criteria.

Polarographic methods for the determination of tungsten are few in number in the literature. In 4 - 10 M hydrochloric acid, W(VI) gets reduced to W(V) which gets further reduced to W(III) [1]. A medium containing phosphoric acid and sulphuric acid has been used for the differential pulse polarographic (DPP) determination of tungsten in nuclear fuels [2]. Catalytic reduction of W(VI) in the presence of hydrogen peroxide or chlorate has also been reported [3-7] but the shape of the wave was often unsatisfactory. Recently, a report appeared for analysis of W(VI)-2- mercapto-benzo-thiazole complex based on the catalytic hydrogen current in polarography [8]. In the present work, the differential pulse polarographic behaviour of W(VI) in a medium containing 8-hydroxyquinoline (oxine) and sodium chlorate has been reported and the most suitable conditions for the determination of tungsten are described. The mechanism of the electrode process is examined using DPP diagnostic criteria.

EXPERIMENTAL

Apparatus and Reagents

The polarograph and the cell assembly was described earlier [9]. For DPP measurments, the pulse duration was 0.04 s and the pulse amplitude was 50 mV. The rate of flow of mercury was 1.862 mg/s. The droptime was mechanically controlled. All the polarograms were recorded at 25° C.

All chemicals were of analytical reagent grade. A standard solution of tungsten (1000 μ g/ml) was prepared from sodium

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tungstate and diluted as required. Oxine solution (0.10 M) was prepared in 0.25 M hydrochloric acid. Sodium chlorate solution (1.0 M) was prepared in water.

Required volumes of individual components were added to the cell, pH was adjusted and test solution was prepared in the cell. Solution was deaerated and polarograms recorded.

RESULTS AND DISCUSSION

Differential pulse polarograms of tungsten.

The peak current in DPP of W(VI) was of poor sensitivity in oxine medium at pH 1.7 (Fig. 1A). In presence of both chlorate and oxine at the same pH, the reduction peak increased in height (Fig. 1B). Enhancement of the current was observed to be about 30 times.

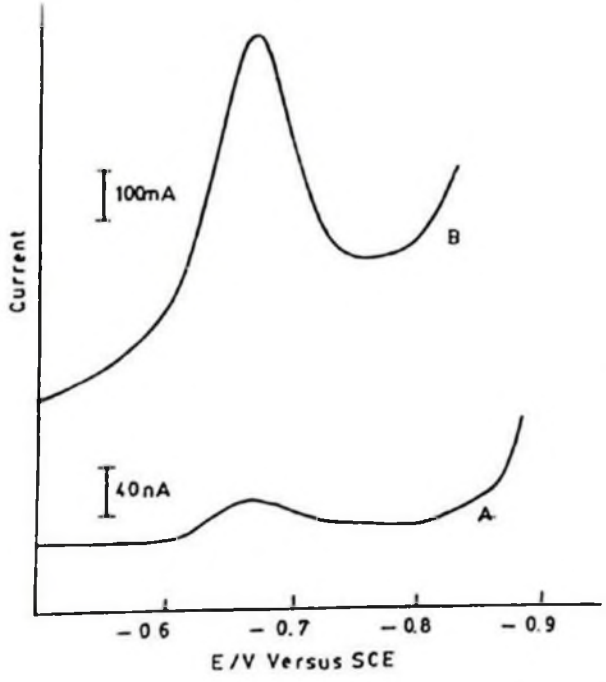


Fig. 1 Effect of Chlorate on DPP of W(VI) in oxine medium
DPP conditions: t = 0.5s; ΔE = 50 mV; scan rate = 2 mV/s. [W(VI)] = 3.0 ppm; pH 1.7 ± 0.1
(A) 0.005 M oxine; (B) 0.005 M oxine + 0.05 M sodium chlorate.

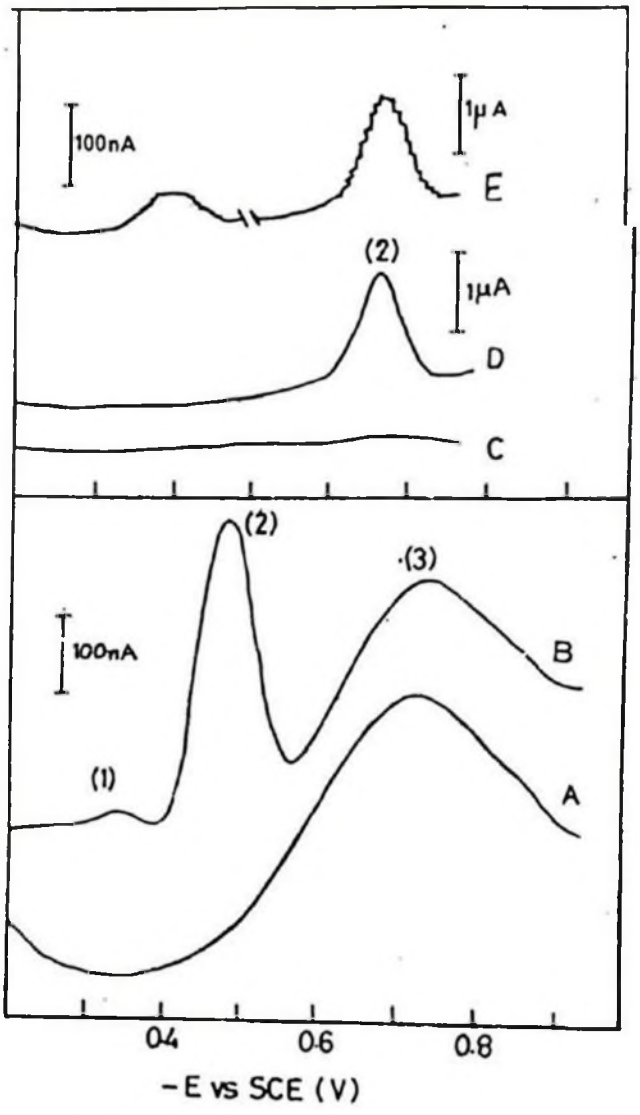


Fig.2 Effect of Oxine on DPP of W(VI) in chlorate medium
DPP conditions: t = 0.5 s; ΔE = 50mV; scan rate = 12 mV/s; pH 1.7 ± 0.1
(A) 0.10 M sodium chlorate
(B) W(VI) = 5.0 ppm in 0.10 M chlorate
(C) 0.005 m oxine in 0.10 M chlorate
(D) W(VI) = 5.0 ppm in 0.10 M chlorate + 0.005 M oxine (E) Same as D Note that the first peak height is recorded at different sensitivity

Sodium chlorate solution at pH 1.7 gave a DPP with a large, broad peak around -0.7 V (Fig. 2A). Recording a polarogram immediately after adding tungstate to this medium showed two peaks (-0.35 V and -0.50 V) in addition to the chlorate peak (Fig.2B). The peak at -0.5V had slightly higher sensitivity but the peak current decreased rapidly with time. Subsequent runs showed lower peak height. (This may be due to hydrolysis of W(VI) at this low pH to give different hydrolysed species). On adding oxine to chlorate medium at pH 1.7, both peaks shifted to more negative potentials (-0.4 and -0.68 V) and also increased in height (Fig.2E. It should be noted that the two peaks were recorded at different sensitivites. If the two peaks are recorded at the same sensitivity, the first peak almost becomes un-noticeable Fig 2D). The peak heights of these do not decrease with time. They are reproducible with time. W(VI) appears to get stabilized due to complexation with oxine and does not undergo hydrolysis.

The first peak (around -0.4 V) could be due to the reduction of W(VI) to W(V) and the second (around -0.68 V) could be due to the reduction of W(V) to W(III). This second peak was chosen for the determination of tungsten because this had a well-defined shape and greater sensitivity.

Optimisation of Supporting Electrolyte

The effect of varying pH (in the range 1.4-2.5) on the peak potential and current of the second peak in DPP of

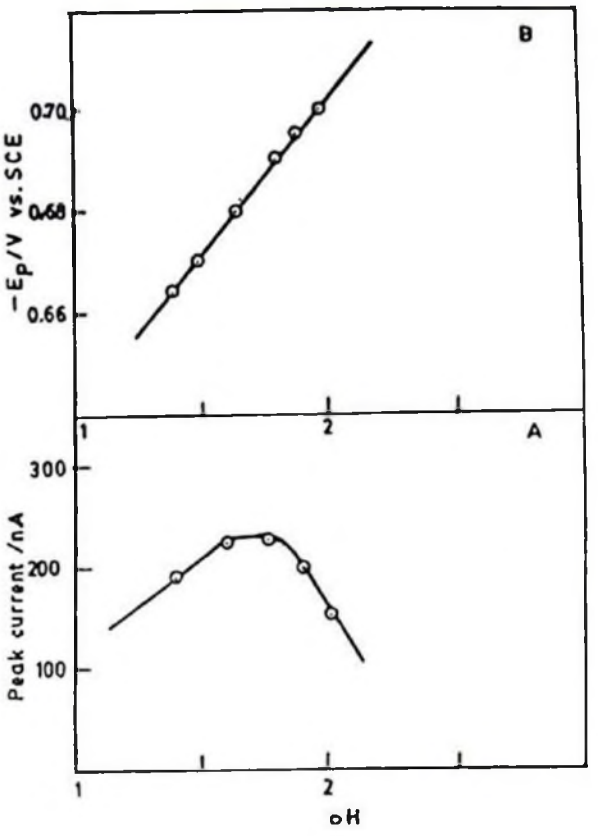


Fig.3 Effect of pH on the peak current (A) and the peak potential (B) of the DP catalytic current of W(VI)
medium oxine (0.005 M) and chlorate (0.05M)
W(VI) = 1.0ppm; t = 0.5s; ΔE = 50 mV

W(VI) is shown in Fig.3. The peak potential shifted linearly towards more negative values with increasing pH. The slope ΔEp/ΔpH was -60 mV/pH unit. The peak current increased, reached a maximum at pH 1.6-1.8 and decreased thereafter. So a pH of 1.7 ± 0.1 was selected as the optimium value for the present study.

The effect of oxine concentration on the DPP of W(VI) has been examined in a medium of 0.05 M sodium chlorate at pH 1.7. The height of the second peak increased with oxine concentration and became a constant above 0.005 M oxine. So in further studies oxine concentration was maintained at 0.005 M.

In 0.005 M oxine medium adjusted to pH 1.7, the effect of chlorate concentration on the current of the second peak in DPP of W(VI) is shown in Fig 4. Initially the current increased rapidly with chlorate concentration, but increase was only slight above 0.05 M chlorate. (Fig.4A). Further at higher concentration of chlorate, the irreversible reduction of chlorate gave rise to a broad peak at about -0.72 V (Fig.2A). This interferes with the determination of tungsten at very low concentrations. So higher chlorate concentration has to be avoided. Hence 0.05 M chlorate was chosen as the optimum concentration for the determination of tungsten by this method.

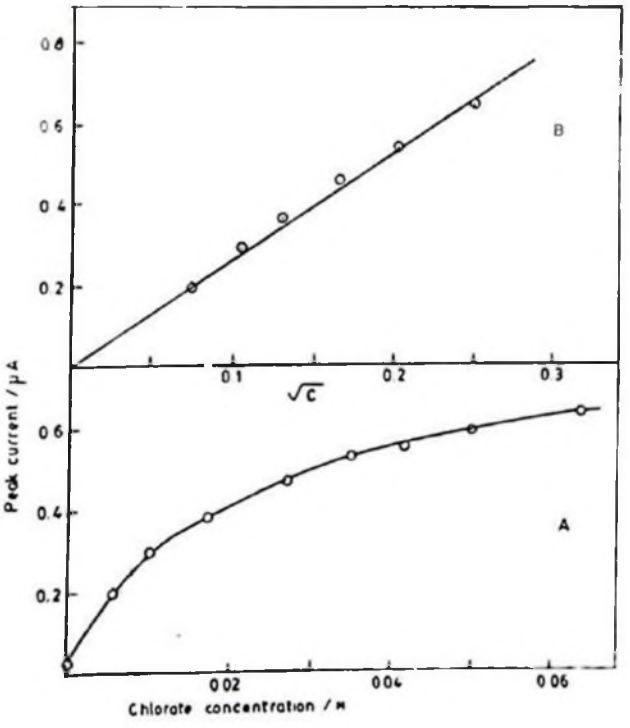


Fig.4. Effect of chlorate concentration on the peak current of W(VI)
S.E. 0.005 M oxine at pH 1.7 ± 0.1 tungsten = 1.0 ppm.
A peak current vs [chlorate]; B. peak current vs ([chlorate]) 1/2.

So a medium containing 0.05 M chlorate, 0.005 M oxine and adjusted to pH 1.7 ± 0.1 was the supporting electrolyte used in the present method.

Mechanism of the Electrode Process

Tungstate is known to be reduced in two steps in strongly acidic, aqueous medium. The first is due to reduction of W(VI) to W(V) and the second is due to reduction of W(V) in W(III) [10]. It is reported that the first is an irreversible step and the second is reversible.

The second peak in the DPP of W(VI) has been selected in the present study. It is already seen that this represents reduction of W(V) to W(III). W(VI) forms 1:2 complex of the type $WO_2(Ox)_2$ with oxine. We found that this complex gets reduced at DME in two steps - first to $WO(OH)(Ox)_2$ and this gets further reduced to $W(OH)(Ox)_2$.

Reduction step of W(V) to W(III) in acid medium is reported to be reversible [10]. In the present case, the height of this

peak current is unduly high. A logarithmic analysis of the correponding DC reduction step [W(V) -> W(III)] in this medium showed that the electrode process is irreversible with a $n\alpha$ value of 1.47. This value can also be obtined from the DPP using the equation $\alpha n = 90/W_{1/2}$ where $W_{1/2}$ is the half peak width at low pulse amplitude. The $W_{1/2}$ of the DPP of tungsten peak was 64 mV at ΔE = 10 mV. The calculated value of $n\alpha$ thus works out to be 1.4. This value agrees well with the value obtained by DC polarogram. Since this peak current corresponds to the reduction of W(V) to W(III), the number of electrons involved in the electron transfer step is 2.

The dependence of peak potential on pH of the medium has already been shown to be linear with a slope of -60 mV/ pH unit (Fig.3B). Since n = 2, one can infer from this slope value that two hydrogen ions are participating in the electron transfer step.

Birke et. al.'s DPP diagnostic criteria [11,12] was used to characterise the mechanism of the electrode process. The ratio of anodic to cathodic peak current was 0.60. (For a reversible electrode reaction, this ratio is unity). The difference in peak potential was less than the pulse amplitude. This shows that the electron transfer process is not reversible. Further the peak current of the second step in oxine - chlorate medium is much higher than twice the peak current of the first step. This suggests catalytic nature of the electrode process. This peak current was found to be a linear fuction of the square root of chlorate concentration (Fig. 4B). This is a characteristic of catalytic electrode process. Hence the electrode process is probably an EC (catalytic) mechanism with quasi-reversible or irreversible electron transfer.

From the experimental observations, the following reactions can be proposed for the catalytic wave of W(V) to W(III) in the presence of chlorate and oxine:

$$WO(OH)(Ox)_2 + 2\,H^+ + 2e \longrightarrow W(OH)(Ox)_2 + H_2O \quad ....(1)$$

$$WO(OH)(Ox)_2 + 2\,H^+ + 2e \longrightarrow W(OH)(Ox)_2 + H_2O \quad ....(1)$$

$$W(OH)(Ox)_2 + ClO_3^- + 4\,H^+ \longrightarrow WO(OH)(Ox)_2 + Cl^- + 2H_2O \quad ...(2)$$

We found that in a medium containing 0.05 sodium chlorate and 0.005 M oxine at pH 1.7 ± 0.1, the catalytic current was proportional to tungsten concentrations in the range 0.50 - 10 ppm. A least- squares fit of the peak current vs tungsten concentration data was carried out for a straight line by y-residual minimization. The regressional parameters were : slope = 900 nA/ppm; y-intercept = - 47 nA and correlation coeffecient = 0.997. The slope of the calibration graph decreased above 10 ppm. At concentrations lower than 0.50 ppm, the base current due to the reduction of chlorate interfered.

Procedure of Analysis

An aliquot of the sample solution was transfred into a polarographic cell containing 2.0 ml of oxine (0.1 M) and 1.0 ml sodium chlorate (1.0 M); the pH was adjusted to 1.7 ± 0.1 with dilute sodium hydroxide or dilute hydrochloric acid; diluted to 20 ml; the solution was deaerated by bubbling pure nitrogen and DPP was recorded from -0.50 V to -0.90 V. The DPP conditions used were: pulse time = 0.04 s; pulse amplitude = 50 mV; droptime = 2.0 s. A standard additon of W(VI) was made and DPP was recorded again. Analysis was carried out by standard addition procedure.

Study of Interferences

The effect of other ions on the peak current of tungsten was investigated. It was found that 20 - fold amounts of Al(III) and Fe(III) did not interfere with the determination of tungsten. 10 - fold amounts of Ti(IV) and V(V) also did not interfere. There was no interference from equal quantities of Cu(II), Pb(II), Cd(II) and Zn(II). Even though these elements form complexes with oxine, the complexation was negligible at the experimental pH of measurement. Molybdenum(VI) - even in trace amounts - gave rise to a large peak at a more positive potential but it did not overlap with the tungsten peak; the peaks were well-separated. The peak current of tungsten was not affected by the presence of equal quantities of Mo(VI) but resulted in slight error for the measurement of tungsten peak by distorting the base current.

Determination of Tungsten in Steel Samples

The standardised procedure was checked with two BCS standard steel samples. The sample treatment was carried out as given below:

An accurately weighed amount (100 mg) of the sample was dissolved in 20 ml of 1:5 (v/v) sulphuric acid and 5 ml 1:5 (v/v) phosphoric acid. 1 to 2 ml of nitric acid was added to oxidize any carbon present, boiled for a few minutes, made up to 100 ml with distilled water. 1 ml aliquot was used for the determination of tungsten in the sample. When the iron to tungsten ratio in the sample was greater than 20 (as in BCS 281), excess iron was removed by solvent extraction with methyl isobutyl ketone in 6 M hydrochloric acid.

Table 1

Determination of Tungsten in Steels

Sample	Tungsten, %		Standard deviation
	Certified	Found*	
BCS 486	6.48	6.40	0.26
BCS 281	0.70	0.68	0.04

* Mean of 6 replicate measurements

The results obtained for the standard steel samples are given in Table 1. The relative standard deviation for 6 replicate measurements was found to be about 5%. The method is suitable in test solutions containing 0.5 to 10 ppm tungsten.

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