Enhanced sensitivity for the differential pulse polarographic determination of Mo(VI) based on adsorption catalytic current

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Abstract. A differential pulse polarographic (DPP) method based on the adsorption catalytic current in a medium containing chlorate and 8-hydroxyquinoline (oxine) is suggested for the determination of molybdenum(VI). Experimental conditions such as pH and the composition of supporting electrolyte have been optimized to get a linear calibration graph at trace levels of Mo(VI). The sensitivity for molybdenum can be considerably enhanced by this method. The influence of possible interferences on the catalytic current has been investigated. The sensitivity of the method is compared with those obtained for other DPP methods for molybdenum. A detection limit of 1.0×10^{-8} mol/L has been found.

Introduction

By coupling of catalytic and adsorption processes remarkably low detection limits could be obtained during the stripping voltammetric determination for a number of elements [1–6]. Based on this principle ultra trace levels of Ti, Mo, Pt, W, and V have been determined using stripping voltammetric procedures. Although the same principle can be used to achieve an enhanced sensitivity in DPP, only a few applications have been reported in the literature [7–9]. A highly sensitive polarographic method has been reported for Mo(VI) in the presence of chlorate, benzilic acid and 2-methyl-8-quinolinol [7]. Barrado et al. have described a sensitive DPP method for the determination of Mo(VI) in a medium containing salicylaldoxime and bromate [8].

In this study, the DP polarographic characteristics of Mo(VI) in the presence of chlorate and oxine is studied systematically to develop a highly sensitive DPP method for the determination of Mo(VI).

Experimental

The polarograph had been described earlier [10]. For DPP measurements, a pulse duration of 0.04 s and a pulse amplitude of 50 mV was chosen. All reagents used were of analytical reagent grade. A standard solution of Mo(VI) (1000 μg/g) was prepared from sodium molybdate and diluted as required. Oxine (0.10 mol/L) was solved in 0.25 mol/L HCl and NaClO$_3$ (1.0 mol/L) in water.

Procedure. Transfer a suitable aliquot of the sample solution into a polarographic cell containing 1.0 ml of 0.1 mol/L oxine and 2.0 ml of 1.0 mol/L sodium chlorate and adjust the pH of the solution to 2.0 ± 0.1. Dilute the solution to 20 ml. Deaerate

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the solution and record the polarogram from –0.10 to –0.60 V vs. SCE. Repeat the procedure after a standard addition of Mo(VI).

Results and discussion

Figure 1 shows the differential pulse polarograms of Mo(VI) in media containing oxine *(A)*, chlorate *(B)* and a mixture of oxine and chlorate *(C)*. In a medium of 0.005 mol/L oxine at pH 1.8 ± 0.1, two peaks arise for Mo(VI) at –0.175 V and –0.315 V vs. SCE. In a medium containing 0.05 mol/L chlorate at pH 1.8 ± 0.1, Mo(VI) gives two peaks at –0.22 V and –0.40 V. These two peaks have a catalytic character because their sensitivities are very much higher than those of diffusion controlled currents obtained in the absence of chlorate. In the presence of oxine and chlorate, the peak currents of both peaks are increased (Fig. 1 *C*). Peak (2) is more sensitive than peak (1) and hence this peak current is chosen for the determination of trace levels of Mo(VI).

The effect of pH on the second peak of Mo(VI) in a S.E. of 0.005 mol/L oxine + 0.05 mol/L chlorate was investigated. The peak current increases with increase in pH up to pH 2.2, attains a maximum in the pH range 2.2–2.4 and decreases at higher pH values. The peak potential shifts in the negative direction linearly with an increase in pH with a slope of –60 mV. This shows that hydrogen ions are involved in the reduction process of Mo(VI) at DME.

Influence of the concentrations of chlorate and oxine. The peak current of the second Mo(VI) peak chosen increases non-linearly with an increase in chlorate concentration. However, the peak current is found to be a linear function of the square root of chlorate concentration in the chlorate concentration range of 0.01–0.07 mol/L. This is typical for catalytic electrode processes. The peak current increases with an increase of oxine concentration, reaches a maximum at 0.002 mol/L and remains
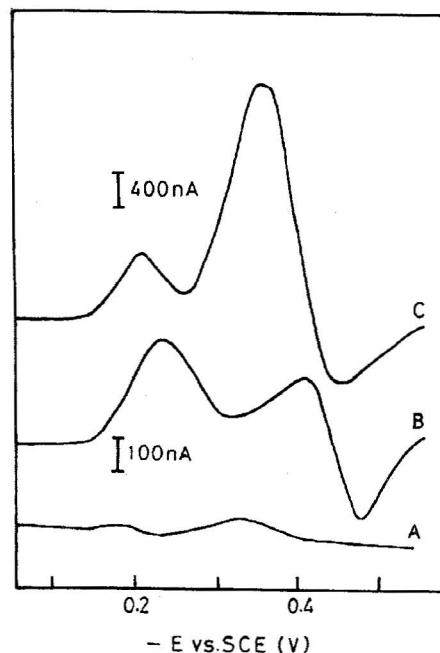

Fig. 1. Differential pulse polarograms of Mo(VI) in S.E.'s of *(A)* 0.005 mol/L oxine, and *(B)* 0.05 mol/L sodium chlorate and *(C)* 0.05 mol/L chlorate + 0.005 mol/L oxine; pH 1.8 ± 0.1; [Mo(VI)] = 0.25 μg/g, DPP conditions: t = 0.5 s; ΔE = 50 mV; h = 75 cm

Table 1. Sensitivity of DPP-methods for Mo(VI) using different electrolytes

Supporting electrolyte	Sensitivity (μA/mM)	Enhancement factor
0.25 mol/L H_2SO_4	8.0	
1.0 mol/L $NaNO_3$ + 0.25 mol/L H_2SO_4	96.0	12
0.05 mol/L chlorate; pH 1.8 ± 0.1	290.4	36
0.005 mol/L oxine; pH 1.8 ± 0.1	19.2	2.4
0.005 mol/L oxine + 0.5 mol/L nitrate; pH 1.8 ± 0.1	3840.0	480
0.005 mol/L oxine + 0.05 mol/L chlorate; pH 1.8 ± 0.1	7840.0	980

[Mo(VI)] = 0.1 μg/g; t = 2.0 s; ΔE = 50 mV

constant thereafter. Based on these results, a medium of 0.05 mol/L chlorate and 0.005 mol/L oxine at pH 2.0 was chosen for the determination of Mo(VI).

The temperature coefficient calculated by Meites' method [11] over the range 25–40°C is found to be 7.5%/°C.

Effect of other ions on the peak current of 0.1 μg/g of Mo(VI). 10-fold amounts of Cu(II), Pb(II), Cd(II), Ni(II), Zn(II) and Co(II), 100-fold amounts of Al(III) and 10-fold amounts of Fe(III) did not interfere. A slight increase in peak current was observed in the presence of 100-fold amounts of Fe(III). Even though Al(III) and Fe(III) are known to form complexes with oxine, no complex formation at the experimental pH of 2 takes place.

A linear calibration graph was obtained in the range of 0.002–0.20 μg/g Mo(VI) using the following DPP conditions: t = 2.0 s and ΔE = 50 mV. A least squares fit of the peak current versus molybdenum concentration data was carried out by y-residual minimization. The regressional parameters obtained are: slope = 81.72 μA/ppm; y-intercept = 1.66 μA; and the correlation coefficient = 0.9960.

The sensitivity for Mo(VI) obtained by this method based on adsorption catalytic effect was compared with those of other DPP methods and the results are given in Table 1. The enhancement in sensitivity obtained in the mixed medium of oxine and chlorate is found to be nearly 1000-fold in comparison to 0.25 mol/L H_2SO_4. The detection limit evaluated from the standard deviation of the blank was found to be 1.0×10^{-8} mol/L.

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Field determination of iodide in water

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Abstract. A simple, fast and sensitive spectrophotometric method for the quantification of iodine and iodide in waters is described. Firstly iodide has been oxidised by sodium nitrite to iodine in HCl medium and the resulting I_2Cl^- has been preconcentrated into toluene. This can be subsequently determined in the extract with brilliant green. A ten-fold preconcentration is obtained, the molar absorptivity is (4.2×10^4) l mol^{-1} cm^{-1} at 635 nm. A detection limit of 4 ng/ml iodide in water can be reached. The effect of common anions and cations have been investigated. The method has been applied to the determination fo free iodine, total iodine and iodide in river, pond and well water.

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Introduction

The field determination of iodine at trace levels present in natural waters, foods, and soils has been considered of great importance to control the disease "goiter" occurring due to iodine deficiencies [1]. Several methods i.e. colorimetric, chromatographic techniques have been reported for determining iodide