



SIMULTANEOUS DETERMINATION OF TUNGSTEN (VI) AND MOLYBDENUM (VI) FROM CATALYTIC REDUCTION OF IODATE

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ABSTRACT

A simple method for the simultaneous determination of Micro quantities of Tungsten and Molybdenum is developed based on the Catalytic Reduction of Iodate at the d.m.e. The Catalytic wave consists of a peak at -1.65 V vs SCE. Interference of various anions and cations has been investigated. A possible reaction mechanism has been proposed.

Keywords: D.C.Polarography, Iodate, Acetic acid-Sodium acetate buffer, d.m.e, height of the mercury column, Catalytic wave, SCE, Tungsten(VI), Molybdenum(VI).

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INTRODUCTION

Many Inorganic redox systems involving Transition Metal ions in higher valent state are known to Catalyse the Polarographic reduction of oxidants such as Hydrogen peroxide, Chlorate, Perchlorate, Bromate and Iodate. These Catalytic waves are exploited to develop sensitive methods for the determination of the Metal ions present in trace quantities¹⁻⁵. The present paper deals with the simultaneous determination of trace quantities of Tungsten and Molybdenum exploiting the effect of one Metal ion on the other in the Polarographic Catalytic reduction of Iodate.

EXPERIMENTAL

Reagents

All chemicals used were of analytical-reagent grade. Potassium iodate solution (0.1M) prepared in conductivity water with appropriate dilution is used. A 0.2 M Sodium acetate and acetic acid buffer solutions of different pH have been employed in the investigations.

Apparatus

A CL-25 pen recording d.c. polarograph (ELICO, Hyderabad, India), an ELICO Model CL-10 pH meter and a Lingane-type H-cell were employed. The voltages were measured against a saturated calomel electrode. Pure Nitrogen gas is passed through the apparatus for about 15 minutes to remove dissolved oxygen

Recommended procedure

1-12.5 ml of Tungsten (VI) at 1×10^{-7} M concentration, 1ml of Molybdenum (VI) of 1×10^{-2} M, 2.5 ml of Iodate of 2×10^{-2} M concentration and a required volume of distilled water in a 25 ml standard flask so that the total volume is always constant. The solution is made up to the mark with a 0.2 M acetate-acetic acid buffer of pH 5.0. The contents of the flask are transferred into the Polarographic cell after thorough shaking. Hydrogen gas is passed for about 15 minutes to remove dissolved oxygen and then the Polarogram is recorded.

RESULTS AND DISCUSSION

Addition of Molybdenum(VI) to Tungsten(VI)-Iodate system caused greater enhancement in the Peak Current (Fig1). This effect has been exploited for the simultaneous determination of trace quantities of

both metal ions. The effect of the concentration of Tungsten(VI), Molybdenum(VI) and height of the mercury column are presented in the tables 1, 2 and 3 respectively.

Non-dependance of the Peak current on mercury column height indicates that the wave has kinetic nature. Abnormal currents and kinetic nature of wave suggest the catalytic nature of the wave. Tungsten (VI) is known to exist as hydrogen hexatungstate in weakly acidic solutions⁶ (between pH 4 and 6). Orlemann and Kolthoff⁷ reported that the reduction of Iodate in acid solutions (pH 1.0 to 5.5) produces Iodic acid. Tungsten present in the form of hydrogen hexatungstate is known to form polyacids with silicic, boric and phosphoric acids. The reduction of an intermediate species involving hydrogen hexatungstate and iodic acid analogous to tungstosilicic acid and its regeneration by a fast chemical oxidation by Iodate is presumed to be responsible for the catalytic wave in the case of Tungsten(VI). It is known that tungsten forms heteropolyacids⁸ of the type $[\text{MoW}_{11}\text{O}_{40}\text{H}_2]^{6-}$ with Molybdenum(VI). It is known that this heteropolyacid undergoes reduction at the d.m.e.⁹. It is suggested that the formation of Molybdotungstate is responsible for the enhancement in the catalytic current. This enhancement in the peak current is found to be linear with the concentration of Tungsten(VI) in the range 4×10^{-9} to 5×10^{-8} M as well as 1×10^{-6} to 1×10^{-5} M of Molybdenum(VI).

Interference studies

It was found that the common anion such as chloride, bromide, iodide, sulphate, carbonate, ferricyanide, thiocyanate do not interfere in the determination up to 10 fold excess of Tungsten(VI) concentration. Cu(II), Co(II), Cd(II), Cr(VI), Cr(III), Zn(II), Mn(II), U(VI), Zr(IV), EDTA, tartrate and citrate interfere if their respective concentration exceed 10 fold of Tungsten(VI).

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REFERENCES

1. V. Suryanarayana Rao and S. Brahmaji Rao, *Z. Anal. Chem.*, **294**(5), 414 (1979)
2. V.S.N. Rao and S.B. Rao, *Talanta*, **26**, 502 (1979)
3. R. Ramachandra Murthy and V. Suryanarayana Rao, *Analyst*, **109** (8), 1111 (1984).
4. R. Ramachandra Murthy and V. Suryanarayana Rao, *Analytical Letters*, **18** (A12), 1479 (1985).
5. R. Ramachandra Murthy and V. Suryanarayana Rao, *Fresenius Z. Anal. Chem*, **323**, 495 (1986).
6. H. Remy, *Treatise on Inorganic Chemistry Vol.II*, 177 Elsevier, New York (1970)
7. E.F. Orlemann and I.M. Kolthoff, *J. Am. Chem. Soc.*, **64**, 1044, 1970 (1942).
8. S.G. Mairanovskii, *Catalytic and Kinetic Waves in Polarography*, Plenum Press, New York (1968)
9. Myriam Lamache et al., *J. Electroanal. Chem.*, **67**, 81 (1976)

Table-1: Effect of the concentration of Tungsten(VI) on the peak current in presence of Molybdenum(VI)
[Mo(VI)] = 4×10^{-4} ; $[\text{IO}_3^-]$ = 20×10^{-4} ; pH = 5.0

Concentration of Tungsten (VI) M	Peak Current μA	Peak Potential (-V vs SCE)
4×10^{-9}	26.0	1.65
1×10^{-8}	30.2	1.65
2×10^{-8}	34.5	1.65
3×10^{-8}	38.8	1.65
4×10^{-8}	42.3	1.65
5×10^{-8}	47.0	1.65

Table-2: Effect of concentration of Molybdenum (VI) on the peak current in presence of Tungsten (VI)

$$[W(VI)] = 4 \times 10^{-4}, [IO_3^-] = 20 \times 10^{-4}, pH = 5.0$$

Concentration of Molybdenum (VI) M	Peak Current μA	Peak Potential (-V vs SCE)
1×10^{-6}	6.0	1.65
8×10^{-6}	12.2	1.65
16×10^{-6}	18.5	1.65
24×10^{-6}	24.6	1.65
32×10^{-6}	31.0	1.65
40×10^{-6}	37.5	1.65

Table-3: Effect of the Mercury column height on the peak current in presence of Tungsten(VI) and Molybdenum(VI)

$$[W(VI)] = 4 \times 10^{-8}; [IO_3^-] = 20 \times 10^{-4}; pH = 5.0$$

Height of Mercury Column (Cms)	Peak Current μA	Peak Potential (-V vs SCE)
80	42.0	1.65
70	42.2	1.65
60	42.5	1.65
50	42.0	1.65
40	42.5	1.65
30	42.0	1.65

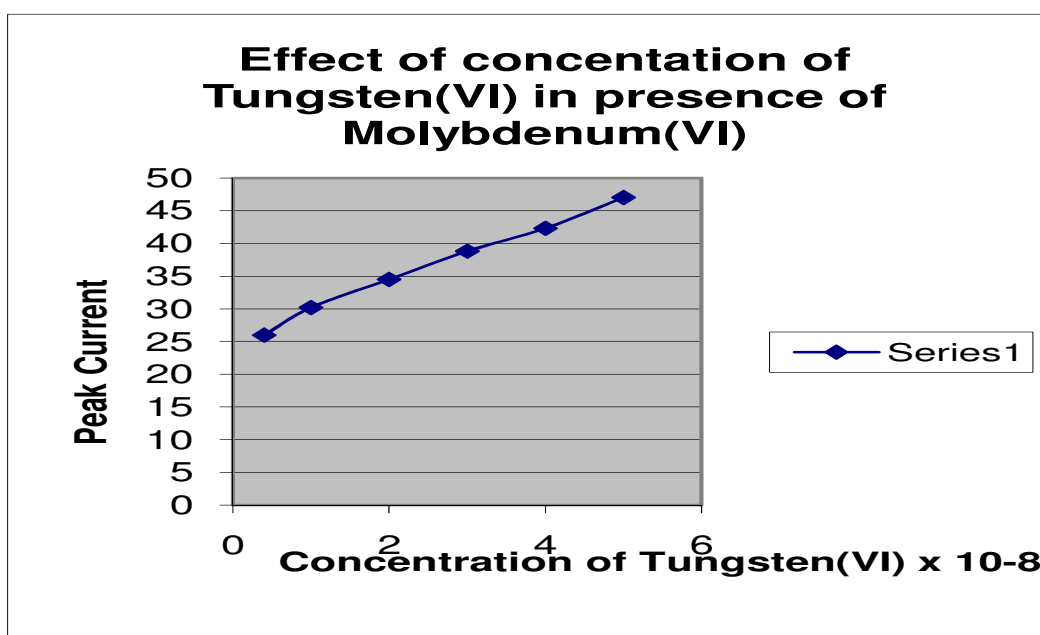


Fig.-1

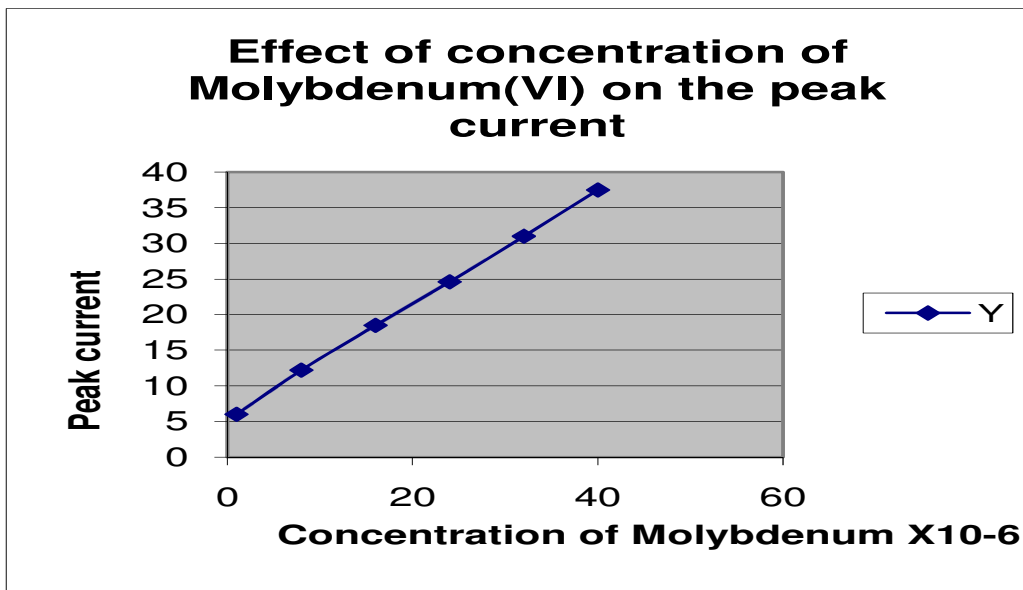


Fig.-2

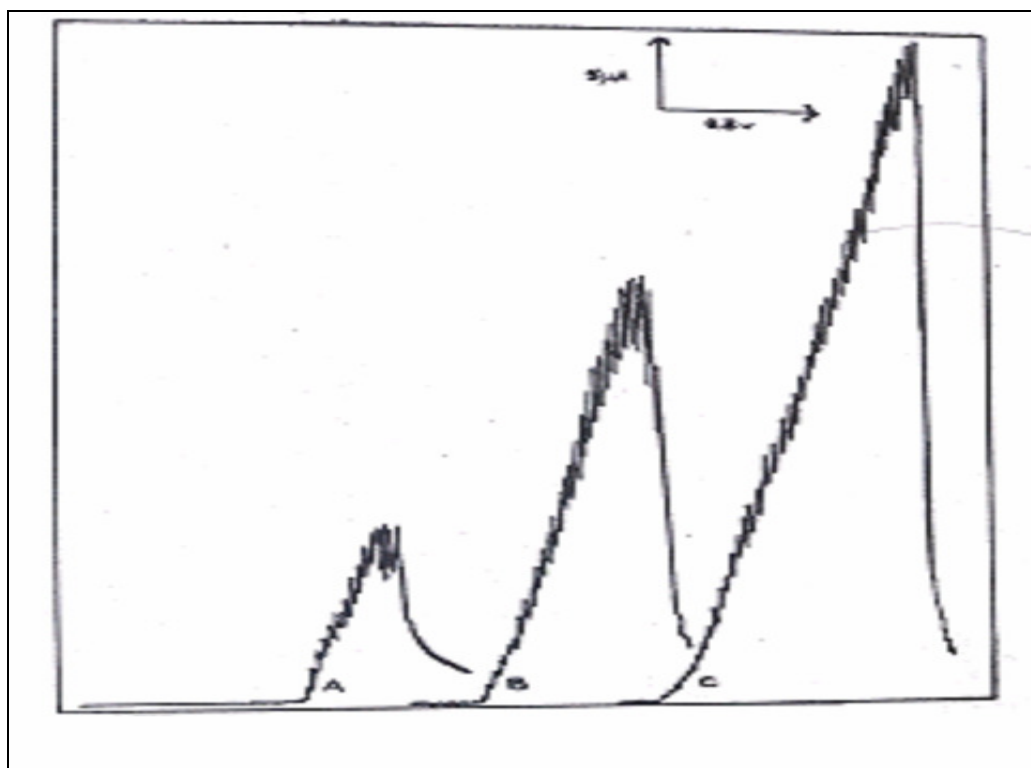


Fig.-3: Effect of Molybdenum (VI) on the Tungsten (VI) iodate system. Tungsten to Molybdenum ratio : (A) 1:1, (B) 1:10 and (C) 1:100
[W(VI)] = 4×10^{-6} ; [IO₃⁻] = 20×10^{-4} ; pH = 5.0

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