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Pyrocatechin Violet—A Selective and Sensitive Reagent for the Spectral and Amperometric Determination of Cu(II)

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Electroanalytical and spectral techniques have been successfully utilized for the low level detection of Cu(II). These methods proved that Cu(II)-PV stoichiometric ratio is 1 : 2 with stability constant for the said complex log $K_s = 8.4183$. The free energy of formation $\Delta G°$ is found to be -11.54 kcal $mole^{-1}$. Spectral studies have been carried out at 630 nm. However, the amperometric titrations could be successfully performed at −1.28 V *vs.* SCE, the plateau potential of pyrocatechin violet. The pHs were mentioned at 5.0 ± 0.01 with Walpole buffer. The reverse L-shaped curves were observed. Ultramicro and microgram quantities of Cu(II) could be estimated without any hindrancés; proposed methods are rapid, convenient, accurate and sensitive under the prescribed experimental conditions.

INTRODUCTION

Xylenol orange, methyl orange and methyl thymol blue have been utilized as an amperometric and spectral reagents for the low level detections of many transition and rare metals[1–3]. In continuation with our work on trace estimations using newer procedures and electroanalytical method, the present paper reports the use of pyrocatechin violet using amperometric methods and photometric methods. The results obtained are summarized and critically discussed along with the various experimental conditions.

EXPERIMENTAL

The chemicals used are of AnalaR or extra pure quality. The solution of pyrocatechin violet was prepared by dissolving requisite amount of this reagent in bidistilled water and its strength was checked up by photometric method[4]. The solution of Cu(II) was prepared by dissolving AR grade $CuSO_4 \cdot 5H_2O$ in doubly distilled water and standardized. The Walpole buffer was prepared using sodium acetate and acetic acid of BDH grade.

The photometric studies were carried out on systronic-112 model of photoelectric colorimeter at 630 nm. A manually operated polarographic set up was used for amperometric titration. The capillary had a value of $m^{2/3}t^{1/6} = 2.31$ $mg^{2/3}$ $sec^{-1/2}$ at 35 cm effective height of Hg column. The polarograms of pyrocatechin violet in acetate buffer of pH 5 revealed four stage reduction and the plateau potential was found to be −1.28 V *vs.* SCE, which were fixed for each of the amperometric titrations.

RESULTS AND DISCUSSION

Tables 1 and 2 suggest that Cu(II) forms a coloured complex with pyrocatechin violet. The study revealed the formation of the 1:2 complex. Vosburgh and Cooper's method was used to study the nature of the complex formed[5]. λ_{max} was found to be at 630 nm. Job's method of continuous variation[6] and molar ratio method were applied for the formation of the complex, which revealed 1:2 stoichiometry. The following values were obtained $\alpha = 0.2608$, $K_s = 2.63 \times 10^8$ and hence $\log K_s = 8.41$ along with $\Delta G° = -11.5$ kcal $mole^{-1}$. Figures 1 and 2 suggest formation of the complex and hence the above data.

TABLE-1
Cu(II) WITH PYROCATECHIN VIOLET (JOB'S METHOD)

($\lambda_{max} = 630$ nm)

S. No.	Metal solution Cu(II) 1 mM (mL)	Reagent solution pyrocatechin violet 1 mM (mL)	Buffer solution Sodium acetate + acetic acid (mL)	Optical density	% T
1.	1	8	1	0.84	16
2.	2	7	1	0.92	14
3.	3	6	1	0.98	10
4.	4	5	1	0.96	11
5.	5	4	1	0.90	13
6.	6	3	1	0.66	24
7.	7	2	1	0.52	31

TABLE-2
Cu(II) WITH PYROCATECHIN VIOLET (MOLE RATIO METHOD)

($\lambda_{max} = 630$ nm)

S. No.	Metal solution Cu(II) 1 mM (mL)	Reagent solution pyrocatechin violet 1 mM (mL)	Buffer solution Sodium acetate + acetic acid (mL)	Water (mL)	Optical density	% T
1.	2	1	1	6	0.23	59
2.	2	2	1	5	0.40	41
3.	2	3	1	4	0.58	27
4.	2	4	1	3	0.65	23
5.	2	5	1	2	0.81	16
6.	2	6	1	1	0.87	14
7.	2	7	1	0	0.92	12

Amperometric titrations for the estimation of Cu(II) at pH 5.00 revealed the fact that the minimum amount of 0.31 mg of Cu(II) could be successfully estimated using plateau −1.28 V *vs.* SCE. The test solution of Cu(II) along with buffer at 5.00 pH was taken in a titration cell and the standard solution of pyrocatechin violet was added drop by drop from a semimicro burette. The current was noted with Oswa multiplex spot galvanometer. On plotting galvanometer reading against titrant volume reverse L-shaped curve was obtained. The end point indicated metal to reagent ratio of 1 : 2 which is in good agreement with the results obtained using spectral method. Replicate sets of titrations with different amount of Cu(II) were carried out. It is observed that 100 fold excess of Na^+, K^+, Ca^{2+}, Hg^{2+}, Co^{2+}, Cl^-, ClO_4^-, SO_4^{-2}, NO_3^-, CH_3COO^- do not interfere. However small amounts of Fe^{3+}, In^{3+}, Ac^{3+}, Th^{4+}, Sn^{4+} and rare earth metals could not be tolerated.

From the spectral and amperometric titration studies it is inferred that under the prescribed conditions of pH, plateau, tolerances and other small amounts of Cu(II) can be estimated with high accuracy and precision.

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