CHALCONES AS INORGANIC ANALYTICAL REAGENTS

Part II. Amperometric Estimation of Copper with 2', 3', 4'-Trihydroxy Chalcone

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2', 3', 4'-TRIHYDROXY CHALCONE which was readily prepared by condensing gallacetophenone and benzaldehyde gave an orange-brown precipitate with copper in the cold at a pH of 3·8 to 4·5 but none with cadmium. This reaction was highly sensitive (1,4,00,000) as a spot test.

Experiments carried out by the present author on the polarographic behaviour of this chalcone showed two waves with half-wave potentials at — 1·10 v and — 1·73 v (*vs.* S.C.E.) at pH 4·5 in a 30% aqueous alcohol medium. These values are in close agreement with those reported by Geissman and Friess[1] (— 1·15 v and — 1·77 v *vs.* S.C.E.) The small difference could be traced to the fact that they used 50% isopropyl alcohol at pH 7·5.

The half-wave potential for a solution of copper at a pH 4·5 was found to be — 0·02 v (*vs.* S.C.E.). It was, therefore, considered desirable to investigate the volumetric estimation of copper using this reagent as a titrant, the end point being determined by the amperometric method.

EXPERIMENTAL

Preparation of 2', 3', 4'-Trihydroxy Chalcone

It was prepared by the method of Thomas Eric Ellison.[2] Gallacetophenone (4·2 gm.) and benzaldehyde (2·7 gm.) were dissolved in alcohol (4·5 ml.) and potassium hydroxide (9 gm. in 10 ml. of water) was added. The mixture was kept at 60° C. for three hours and then poured into dilute hydrochloric acid. The chalcone separated at first as a brown oil which slowly solidified. It was repeatedly crystallised from 75% methyl alcohol,

animal charcoal being used to remove a slightly fluorescent, dark impurity, and was obtained as orange-yellow prisms, containing methyl alcohol of crystallisation. After drying at 110° C., it melted at 165–166° C. It was practically insoluble in water but readily soluble in alcohol and acetic acid.

Reagents

Chalcone solution.—Standard solutions of the chalcone were prepared from the recrystallised and dried samples. Accurately weighed quantities were dissolved in rectified spirit and the solution made up to a known volume. Three different concentrations (0·2[illegible]%, 0·176% and 0·2736%) of the reagent were employed in this investigation.

Copper sulphate.—0·01 M solution was prepared by accurately weighing 1·249 gm. of A.R. quality copper sulphate, dissolving in water and making up to 500 ml.

Cadmium solution.—0·01 M solution was prepared by accurately weighing 0·6663 gm. of A.R. cadmium acetate, dissolving in water and making up to 250 ml. after adding a little acetic acid.

Gelatin solution.—A 0·1% aqueous solution of gelatin was prepared from a B.D.H. sample.

Acetate buffer.—A buffer solution (pH 4·5) was prepared from sodium acetate (0·2 M) and acetic acid (0·2 M).

Apparatus

The direct reading Dr. Lange's Polarometer Model-3 was employed for measurements of voltage and current values. Investigations of the polarographic behaviour of chalcone, copper and cadmium as well as the titrations of the copper solution with the chalcone were carried out in a H-cell of the type designed by Lingane and Laitinen.[3] The saturated calomel electrode (S.C.E) was prepared in the narrow limb. The solution was prevented from entry into the wider limb by means of 4% agar jelly containing 30% potassium chloride placed in close contact with the sintered disc inside the tube connecting the two limbs.

The polarographic behaviour of the chalcone, copper and cadmium were studied in 30% aqueous alcohol medium at pH 4·5 in the presence of 0·01% gelatin. The polarograms are shown in Fig. 1.

The half-wave potentials for the reagent are — 1·10 v and — 1·73 v (*vs.* S.C.E). The values for copper and cadmium are — 0·02 v and — 0·60 v (*vs.* S.C.E.) respectively.

Estimation of Copper

A known volume of copper sulphate solution was pipetted out into a 50 ml. volumetric flask. 0·1% gelatin solution (1 ml.), rectified spirit (15 ml.) were added and made up to 50 ml. with acetate buffer. The solution was then transferred to the titration cell and purified hydrogen was bubbled through it slowly for about five minutes to remove the dissolved oxygen.

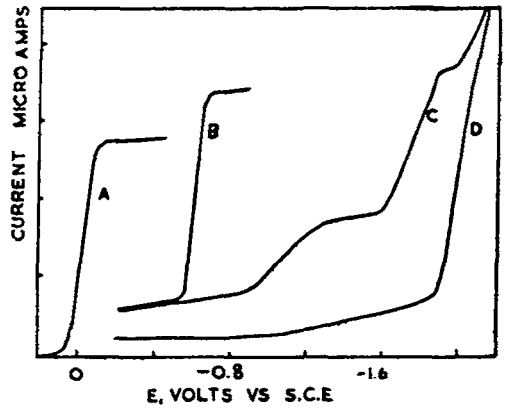


FIG. 1. Curves A, B, C and D represent polarograms for copper, cadmium, reagent and supporting electrolyte respectively.

The dropping electrode was then placed in solution and the droptime adjusted to 2–3 seconds and the voltage applied was kept at — 0·4 v (*vs.* S.C.E). Copper gives a diffusion current at this voltage whereas cadmium requires a much higher value.

The standard solution of the reagent was then added from a micro burette (10 ml.). After each addition a slow stream of hydrogen was bubbled for about one minute to mix the solutions. The current values were noted only after stopping hydrogen. These values were corrected for volume increase and plotted against the volume of the reagent. The equivalence point was determined by drawing straight lines through the experimental points. A typical titration curve is shown in Fig. 2.

The results obtained in a series of titrations are recorded in Table I. The mole ratio of reagent to the copper atoms is given in column III. The

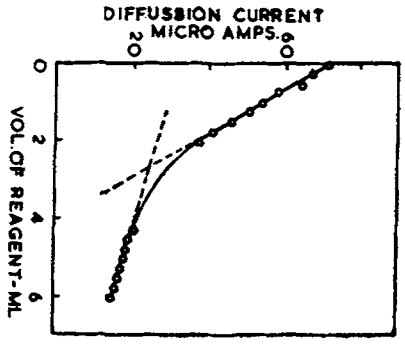
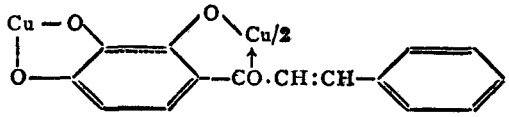


FIG. 2.

TABLE I

Copper (taken) (mg.)	Reagent consumed (mg.)	Copper (gm. atom) / Reagent (gm. mole)	Copper (found) (mg.)	Error (%)
1·290	3·451	1·505	1·285	−0·39
1·586	4·214	1·514	1·578	−0·51
1·904	5·016	1·494	1·906	−0·11
1·934	5·249	1·484	1·937	+0·16
2·137	5·687	1·513	2·124	−0·61
2·538	6·688	1·520	2·498	−1·58
2·854	7·568	1·520	2·829	−0·88
3·173	8·447	1·512	3·170	−0·10
3·225	8·624	1·506	3·221	−0·12
3·668	9·858	1·498	3·684	+0·44
5·076	13·380	1·524	4·996	−1·57
6·345	16·900	1·508	6·311	−0·54

data presented in this column show that 1·0 gm. mole of the reagent reacts with 1·5 gm. atoms of copper and the complex can be given the following structure:



From the data presented above it is obvious that 1·0 to 6·0 mg. of copper can be estimated with an accuracy of ± 1%.

Interference.—The effect of cadmium ions was investigated at pH 4·5 in 30% aqueous alcohol. The results are reported in Table II.

The results show that the errors are within ± 1% with amounts of cadmium of the order of one and a half times that of copper. Although cadmium does not give a precipitate with the reagent at pH 4·5, it has a marked effect on the estimation of copper when the proportion is increased, probably due to co-precipitation.

TABLE II

Copper (taken) (mg.)	Cadmium (added) (mg.)	Copper (found) (mg.)	Error %
2·538	0·562	2·559	+0·83
2·538	1·174	2·559	+0·83
2·538	2·248	2·559	+0·83
2·538	3·372	2·559	+0·83
2·538	4·496	2·662	+4·85
2·538	5·620	2·764	+8·89

SUMMARY

The estimation of copper by titration with 2′, 3′, 4′-trihydroxy chalcone was carried out amperometrically. The titranions were performed in 30% aqueous alcoholic media at pH 4·5 and an applied potential of − 0·4 v

(*vs.* S.C.E.). Results within ± 1% accuracy were obtained for amounts ranging from 1·0 to 6·0 mg. Quantities of cadmium up to 1·5 times that of copper do not interfere.

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REFERENCES

1. Geissman, T. A. and Friess, S. L. .. *J. Amer. Chem. Soc.*, 1949, **71**, 3893.
2. Thomas Eric Ellison .. *J. Chem. Soc.*, 1927, p. 1723.
3. Meites, L. .. *Polarographic Techniques*, Interscience Publications, Inc., New York, 1955, p. 20.