117. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part IV. Naphthidine as Indicator in the Determination of Zinc with Ferrocyanide.*

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Naphthidine can be used as an internal indicator in the titration of zinc with ferrocyanide and gives a more distinct colour change than any of the conventional indicators used for this purpose.

Several indicators have been recommended for the titration of zinc with ferrocyanide, but, in our hands at least, only one, *o*-dianisidine, gives a really satisfactory end-point. This indicator, first used for the titration of ferrous iron with dichromate (Weeks, *Ind. Eng. Chem. Anal.*, 1932, **4**, 127), was later recommended for the titration of zinc with ferrocyanide (Frost, *Analyst*, 1943, **68**, 51). Unfortunately, no information was supplied regarding the accuracy or precision to be expected in the latter titration.

We find that in this titration *o*-dianisidine gives results comparable with those obtained by using diphenylbenzidine (Cone and Cady, *J. Amer. Chem. Soc.*, 1927, **49**, 356; Kolthoff and Pearson, *Ind. Eng. Chem. Anal.*, 1932, **4**, 147) and that no indicator correction is necessary. The colour change (brick-red ⟶ very pale blue-green) is sharper and more easily detectable that that given by diphenylbenzidine.

Tyler (*ibid.*, 1942, **14**, 114) preferred *p*-ethoxychrysöidine to other compounds as indicator for this titration, but we were unable to obtain sharp end-points under his conditions. The present paper summarises our observations on the behaviour of several of the substituted benzidines and related compounds described in our earlier papers (*J.*, 1951 544, 546,) when used as indicators in the titration of zinc with ferrocyanide, and also describes the use of naphthidine for this purpose.

Tyler also used benzidine acetate but found it unsatisfactory as regards colour development and reproducibility.

It was found that benzidine and its 3-methyl and 3 : 3′-diethyl derivatives gave better end-points (yellow ⟶ very pale blue green) than *p*-ethoxychrysöidine or diphenylbenzidine, though not as good as *o*-dianisidine. Naphthidine, however, proved to be better than *o*-dianisidine, especially as regards the colour change (pink-red ⟶ white). No indicator correction was necessary and the indicator was completely reversible. Naphthidine has been recommended as an indicator in the titration of ferrous iron with potassium dichromate (Cohen and Oesper, *Ind. Eng. Chem. Anal.*, 1936, **8**, 306) but we have found that some destruction of the indicator occurs in this particular titration.

Experimental.—Indicator. A 1% solution of naphthidine in glacial acetic acid.

Potassium ferrocyanide solution (0·025M.). 10·557 G. of pure potassium ferrocyanide trihydrate and 0·2 g. of sodium carbonate were dissolved in distilled water, and the solution diluted to 1 litre and kept in a dark bottle.

Potassium ferricyanide solution. A 1% solution in distilled water: it should be kept in a dark bottle and discarded after 2 days.

Zinc solution (0·05M.). 3·269 G. of pure zinc dissolved in an excess of dilute sulphuric acid and diluted to 1 litre.

Titration procedure. A measured amount of zinc solution was transferred to a conical flask and dilute sulphuric acid added to make its concentration about 1N. 1 G. of ammonium sulphate was added per 50 ml. of solution. For this volume, 3 drops of ferricyanide solution and 2 drops of naphthidine indicator were added, and a 10—20% excess of ferrocyanide was run in. The flask was shaken (2—3 minutes) until the suspension became white. The excess of ferrocyanide was then titrated with standard zinc solution to a change from white to pink-red. The end-point was sharp to within 1 drop.

A selection of results is given in the table.

0·05M-Zn taken, ml.	0·025M-$K_4Fe(CN)_6$ added, ml.	Back titration: 0·05M-Zn, ml.	Total 0·05M-Zn, ml. Found.	Calc.	0·05M-Zn taken, ml.	0·025M-$K_4Fe(CN)_6$ added, ml.	Back titration: 0·05M-Zn, ml.	Total 0·05M-Zn, ml. Found.	Calc.
25	40	5·10	30·10	30·00	10	15	1·25	11·25	11·25
25	40	5·05	30·05	30·00	10	15	1·23	11·23	11·25
25	40	5·00	30·00	30·00	10	15	1·20	11·20	11·25
20	30	2·48	22·48	22·50	5	7·5	0·65	5·65	5·63
20	30	2·46	22·46	22·50	5	7·5	0·60	5·60	5·63
20	30	2·50	22·50	22·50	5	7·5	0·60	5·60	5·63
15	25	3·70	18·70	18·75					
15	25	3·78	18·78	18·75					
15	25	3·74	18·74	18·75					

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