348. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part VII.** 3 : 3′-*Dimethylnaphthidine as Indicator in the Titration of Zinc with Ferrocyanide.*

By R. Belcher, A. J. Nutten, and W. I. Stephen.

The properties of 3 : 3′-dimethylnaphthidine (4 : 4′-diamino-3 : 3′-dimethyl-1 : 1′-dinaphthyl) as an indicator in the titration of zinc with ferrocyanide have been investigated. It is more sensitive than naphthidine and the end-point can be detected readily even when 0·001M-solutions are used for the titration.

It has recently been shown (Belcher and Nutten, *J.*, 1951, 547) that naphthidine can be used as an indicator when zinc is determined by titration with potassium ferrocyanide. Since it seemed probable that *m*-substituted naphthidines would behave likewise, the indicator properties of 3 : 3′-dimethylnaphthidine (for preparation, see Fries and Lohmann, *Ber.*, 1921, **54**, 2922) have been investigated. The colour change at the end-point when 0·001M-solutions were used was equivalent in intensity to that obtained with naphthidine when 0·01M-solutions were used; hence it appears to be ten times as sensitive. Moreover, 3 : 3′-dimethylnaphthidine appears to be more stable in solution than both naphthidine and *o*-dianisidine, for the end-point colours obtained with the last two indicators fade after a few hours, whereas that with 3 : 3′-dimethylnaphthidine only shows signs of fading after a few days.

When the zinc and ferrocyanide solutions were diluted to less than 0·01M., it was found necessary to dilute the other requisite reagents (sulphuric acid, ammonium sulphate, and potassium ferricyanide) in order to maintain the same relationships between the zinc and the ferrocyanide.

Titration results are included in the tables. The end-point is sharp to within one drop. No indicator correction is necessary.

Titrations using 0·05M-*zinc solutions.*

0·05M-Zn taken (ml.).	0·025M-$K_4Fe(CN)_6$ added (ml.).	Back titrn. : 0·05M-Zn (ml.).	Total 0·05M-Zn consumed (ml.) : Found.	Calc.	0·05M-Zn taken (ml.).	0·025M-$K_4Fe(CN)_6$ added (ml.).	Back titrn. : 0·05M-Zn (ml.).	Total 0·05M-Zn consumed (ml.) : Found.	Calc.
25	40	4·98	29·98	30·00	15	25	3·74	18·74	18·75
25	40	5·00	30·00	30·00	10	15	1·24	11·24	11·25
20	30	2·52	22·52	22·50	10	15	1·25	11·25	11·25
20	30	2·49	22·49	22·50	5	7·50	0·60	5·60	5·63
15	25	3·7	18·72	18·75	5	7·50	0·63	5·63	5·63

Titrations using 0·005M-*zinc solutions.*

0·005M-Zn taken (ml.).	0·0025M-$K_4Fe(CN)_6$ added (ml.).	Back titrn. : 0·005M-Zn (ml.).	Total 0·005M-Zn consumed (ml.) : Found.	Calc.	0·005M-Zn taken (ml.).	0·0025M-$K_4Fe(CN)_6$ added (ml.).	Back titrn. : 0·005M-Zn (ml.).	Total 0·005M-Zn consumed (ml.) : Found.	Calc.
20	30	2·54	22·54	22·50	10	15	1·30	11·30	11·25
20	30	2·52	22·52	22·50	10	15	1·23	11·23	11·25
15	25	3·69	18·69	18·75	5	10	2·40	7·40	7·50
15	25	3·67	18·67	18·75	5	10	2·48	7·48	7·50

Titrations using 0·001M-*zinc solutions.*

0·001M-Zn taken (ml.).	0·0005M-$K_4Fe(CN)_6$ added (ml.).	Back titrn. : 0·001M-Zn (ml.).	Total 0·001M-Zn consumed (ml.) Found.	Calc.	0·001M-Zn taken (ml.).	0·0005M-$K_4Fe(CN)_6$ added (ml.).	Back titrn. : 0·001M-Zn (ml.).	Total 0·001M-Zn consumed (ml.) : Found.	Calc.
15	25	3·68	18·68	18·75	10	15	1·28	11·28	11·25
15	25	3·70	18·70	18·75	5	10	2·47	7·47	7·50
10	15	1·26	11·26	11·25	5	10	2·45	7·45	7·50

Experimental.

Solutions required.—Potassium ferrocyanide solution : 0·025, 0·0025, *and* 0·0005M. The 0·025M-solution was prepared by dissolving 10·551 g. of potassium ferrocyanide trihydrate and about 0·2 g. of sodium carbonate in water and diluting to one litre. The trihydrate was obtained by recrystallising

* Part VI, preceding paper.

pure potassium ferrocyanide and drying it to constant weight over a saturated solution of sodium chloride and sucrose. The weaker solutions were prepared from the stock 0·025M-solution by appropriate dilution.

Potassium ferricyanide solution: 1, 0·2, *and* 0·1%. Pure potassium ferricyanide was dissolved in water and kept in a dark bottle. The solution was prepared fresh daily.

Zinc sulphate solution: 0·05, 0·005, *and* 0·001M. The 0·05M-solution was prepared by dissolving 3·269 g. of pure zinc in a slight excess of dilute sulphuric acid and diluting to one litre with water. The weaker solutions were prepared by appropriate dilution of the stock 0·05M-solution. The concentration of this solution was checked by determining the zinc as the 8-hydroxyquinoline complex.

Indicator solution. 1 G. of 3 : 3′-dimethylnaphthidine was dissolved with warming in 100 ml. of glacial acetic acid.

Procedure.—Titrations using 0·05M-zinc solutions. The test solution containing zinc was treated with sufficient 2N-sulphuric acid to make its concentration about 1N. in a volume of 50 ml., and 10% ammonium sulphate solution was added to give a total concentration of 1 g. in 50 ml. Four drops of 1% potassium ferricyanide and two drops of indicator were added to this volume. A 10—20% excess of potassium ferrocyanide was run in rapidly with vigorous stirring. After a minute the solution became greyish-green and the excess of ferrocyanide was titrated with standard zinc solution to a change to purple-red.

Titrations using 0·005M-zinc solutions. The procedure described above was repeated except that the final concentration of sulphuric acid in 50 ml. was reduced to 0·2N., and that of ammonium sulphate to 0·4%. Four drops of 0·2% potassium ferricyanide solution and two drops of the indicator were added, and the titration carried out as above.

Titrations using 0·001M-zinc solutions. In this case the final concentration of sulphuric acid in 50 ml. was 0·1N., and that of ammonium sulphate was 0·2%. Four drops of 0·1% potassium ferricyanide and two drops of the indicator were added.

One of us (W. I. S.) is indebted to Messrs. Albright and Wilson Ltd. for a grant enabling him to carry out the work described in this and subsequent papers of this series.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, BIRMINGHAM, 15. [*Received, January 11th,* 1951.]