

**760.** *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part VIII.\* 3 : 3'-Dimethylnaphthidine as Indicator in the Titration of Cadmium, Calcium, and Indium with Ferrocyanide.†*

By R. BELCHER, A. J. NUTTEN, and W. I. STEPHEN.

Cadmium, calcium, and indium can be titrated with ferrocyanide, 3 : 3'-dimethylnaphthidine being used as indicator. Naphthidine, *o*-di-anisidine, and *NN'*-diphenylbenzidine are less satisfactory in these titrations.

It has been shown that naphthidine (Belcher and Nutten, *J.*, 1951, 548) and 3 : 3'-dimethylnaphthidine (4 : 4'-diamino-3 : 3'-dimethyl-1 : 1'-dinaphthyl) (Belcher, Nutten, and Stephen, *J.*, 1951, 1520) can be used as internal indicators in the titration of zinc with ferrocyanide. The present paper describes the behaviour of these indicators in the titration of three other metals which form insoluble ferrocyanides, namely, cadmium, calcium, and indium.

*Titration of Cadmium.*—When the titration was carried out in neutral solution in the presence of ammonium sulphate, both indicators gave very sharp end-points. Both direct titration with standard ferrocyanide, and addition of a known excess followed by back-titration with a standard cadmium solution, gave satisfactory results. Our own preference is, however, for the direct titration method.

Results included in the following table apply to both naphthidine and 3 : 3'-dimethylnaphthidine, similar figures being obtained for both indicators. In all our experiments, the volume of the solution to be titrated was 40 ml. No indicator correction was found to be necessary.

0.05M- Cd, ml.	10% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , ml.	0.05M- K <sub>4</sub> Fe(CN) <sub>6</sub> , ml.	Ratio Cd/K <sub>4</sub> Fe(CN) <sub>6</sub>	0.01M- Cd, ml.	10% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , ml.	0.01M- K <sub>4</sub> Fe(CN) <sub>6</sub> , ml.	Ratio Cd/K <sub>4</sub> Fe(CN) <sub>6</sub>
5	10	4.00, 4.02, 4.00	1.25, 1.24, 1.25	1	10	0.82, 0.80	1.22, 1.25
10	10	8.02, 8.00, 8.00	1.25, 1.25, 1.25	2	10	1.60, 1.62	1.25, 1.24
15	10	12.03, 12.04, 12.00	1.25, 1.25, 1.25	4	10	3.22, 3.23	1.24, 1.24
20	10	16.00, 16.00, 16.03	1.25, 1.25, 1.25	5	10	4.00, 3.98	1.25, 1.26
				10	10	8.03, 8.02	1.25, 1.25

\* Part VII, *J.*, 1951, 1520. † Read, in abstract, at 12th International Congress of Pure and Applied Chemistry, New York, September, 1951.

In acid solution low results were obtained, as shown below, and the titration had to be done very slowly, because the colour of the indicator faded and then reappeared throughout the titration.

0.05M-Cd, ml. ....	5	5	5	5	5	5	5
2N-H <sub>2</sub> SO <sub>4</sub> , ml. ....	20	10	8	6	4	2	1
10% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , ml. ....	10	10	10	10	10	10	10
Acid concn., N. ....	1	0.5	0.4	0.3	0.2	0.1	0.05
0.05M-K <sub>4</sub> Fe(CN) <sub>6</sub> , ml. ....	3.72	3.80	3.84	3.84	3.88	3.94	3.99

An end-point could not be obtained when ammonium salts were absent : either the chloride or the sulphate was satisfactory, but, when large amounts of chloride were present, slightly high results were obtained. The maximum amount of ammonium chloride which could be tolerated was 0.2 g. Amounts of ammonium sulphate ranging between 0.5 and 2.0 g. could be added, but below 0.5 g. the end-points were unsatisfactory and slightly high results were obtained ; in most of our experiments about 1 g. was added. The following results are typical of both indicators.

0.05M-Cd, ml.	10% (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , ml.	0.05M-K <sub>4</sub> Fe(CN) <sub>6</sub> , ml.	0.05M-Cd, ml.	10% NH <sub>4</sub> Cl, ml.	0.05M-K <sub>4</sub> Fe(CN) <sub>6</sub> , ml.
5	2	4.3, 4.34	5	2	4.02, 4.00
5	3	4.25, 4.22	5	4	4.07, 4.06
5	4	4.06, 4.05	5	5	4.12, 4.15
5	5	4.02, 4.00	5	10	4.11, 4.15
5	10	4.00, 4.01	5	20	4.22, 4.24
5	15	4.00, 4.00			
5	20	4.02, 4.00			

Obviously, all metals which form insoluble ferrocyanides will interfere. The only interferences we examined were those of barium and strontium. In the absence of sulphate ions high results were obtained, but, when ammonium sulphate was added barium and strontium sulphates were precipitated and no longer interfered.

Amounts of cadmium ranging from 1 ml. of a 0.1M-solution to 20 ml. of a 0.05M-solution (*i.e.*, 1.12—112.41 mg. of Cd) were titrated. From the titration relationships the precipitate appears to have the composition Cd<sub>5</sub>K<sub>6</sub>[Fe(CN)<sub>6</sub>]<sub>4</sub>, in agreement with the formula assigned to it by Wyruboff (*Ann. Chim.*, 1870, 21, 270).

*o*-Dianisidine and *NN'*-diphenylbenzidine were also tried as indicators in the titration. The respective merits of all four indicators can be summarised as follows :

Indicator	Comment
3 : 3'-Dimethylnaphthidine .....	Very good. End-points sharp at all concentrations
Naphthidine .....	Good. End-points less sharp than with 3 : 3'-dimethylnaphthidine
<i>o</i> -Dianisidine .....	Almost as good as naphthidine
<i>NN'</i> -Diphenylbenzidine .....	Very poor. End-points difficult to detect

*Titration of Calcium.*—When calcium was titrated in neutral aqueous solution, end-points could not be obtained whether ammonium salts were present or not. When, however, ethyl alcohol was added to the solution, satisfactory end-points were obtained, owing to the decreased solubility of the calcium potassium ferrocyanide : the initial concentration should be 85—90% of ethyl alcohol, and 80—85% at the end of the titration. A larger amount of potassium ferricyanide is required than in other titrations of this type, but no correction is necessary.

In solutions of high acid concentration end-points with naphthidine and 3 : 3'-dimethylnaphthidine could not be obtained, although an acidity of 0.05N. with respect to hydrochloric acid could be tolerated.

Amounts of calcium ranging from 1 ml. of 0.01M-solution to 5 ml. of 0.05M-solution (0.4—10.02 mg. of Ca) were titrated satisfactorily. From the titration relationships the formula of the precipitate corresponds to CaK<sub>2</sub>[Fe(CN)<sub>6</sub>]. Results with 3 : 3'-dimethylnaphthidine and naphthidine are given below, the results obtained for both indicators being comparable.

0.05M-Ca, ml.	EtOH, ml.	0.05M-K <sub>4</sub> Fe(CN) <sub>6</sub> , ml.	Ratio Ca/K <sub>4</sub> Fe(CN) <sub>6</sub>	0.01M-Ca, ml.	EtOH, ml.	0.01M-K <sub>4</sub> Fe(CN) <sub>6</sub> , ml.	Ratio Ca/K <sub>4</sub> Fe(CN) <sub>6</sub>
2	35	1.98, 2.00	1.01, 1.00	1	35	1.02, 1.00	0.98, 1.00
4	35	4.00, 4.02	1.00, 0.99	2	35	2.00, 1.98	1.00, 1.01
5	35	5.00, 5.00	1.00, 1.00	4	35	4.00, 4.00	1.00, 1.00
				5	35	5.00, 5.00	1.00, 1.00

The behaviour of the other alkaline-earth metals and of magnesium was also studied. Barium could be titrated by the same procedure, but end-points could not be obtained with strontium and magnesium. When calcium was titrated, however, in the presence of the last two metals, high results were obtained, possibly owing to the formation of other complex insoluble ferrocyanides in which magnesium and strontium were incorporated.

The same four indicators were examined in this titration and their behaviour can be summarised as follows :

Indicator	Comment
3 : 3'-Dimethylnaphthidine .....	Satisfactory. End-point very sharp
<i>o</i> -Dianisidine .....	Poor. End-point difficult to detect
Naphthidine .....	Slightly poorer than <i>o</i> -dianisidine. End-point difficult to detect
<i>NN'</i> -Diphenylbenzidine .....	Very poor. No end-point

Although the end-points with 3 : 3'-dimethylnaphthidine are easily detected, they are not so sharp as those obtained in the cadmium titration.

*Titration of Indium.*—Two methods have been described previously for the titration of indium with ferrocyanide. In one, the titration is effected in acetic acid solution with *NN'*-diphenylbenzidine as indicator (Hope, Ross, and Skelley, *Ind. Eng. Chem. Anal.*, 1936, 8, 51), and in the other, the titration is effected in hydrochloric acid solution and the end-points are determined potentiometrically (Bray and Kirchmann, *J. Amer. Chem. Soc.*, 1927, 49, 2739). The latter workers state that the composition of the indium salt formed is  $\text{In}_5\text{K}[\text{Fe}(\text{CN})_6]_4$ ; but presumably under the conditions of Hope, Ross, and Skelley, the precipitate is of uncertain composition, for the ferrocyanide solution must be standardised against pure indium under the conditions of an actual determination.

In the present investigation it was found that titration could be done in acid solution in the presence of ammonium sulphate or ethyl alcohol, but the ratio  $\text{In} : \text{Fe}(\text{CN})_6$  was 5 : 4.2 instead of 5 : 4 as would be expected from the above formula. In acetic acid solution the end-points with naphthidine, 3 : 3'-dimethylnaphthidine, and *o*-dianisidine were poor and variable, the colours of the first two indicators fading throughout the titration; however, 3 : 3'-dimethylnaphthidine gave much better end-points than *NN'*-diphenylbenzidine.

In neutral solution excellent end-points were obtained and the ratio  $\text{In} : \text{Fe}(\text{CN})_6$  was exactly 5 : 4, corresponding to the above formula. Direct titration was possible, but it was preferable to add an excess of ferrocyanide solution and to back-titrate with a standard indium solution. Amounts of indium varying from 1 ml. of 0.01M-solution to 20 ml. of 0.05M-solution (1.15—114.8 mg. of In) were titrated satisfactorily. Results with 3 : 3'-dimethylnaphthidine are included in the following table.

0.05M-In, ml.	0.05M- $\text{K}_4\text{Fe}(\text{CN})_6$ , ml.	Back-titrn. : 0.05M-In, ml.	Ratio In/ $\text{K}_4\text{Fe}(\text{CN})_6$	0.01M-In, ml.	0.01M- $\text{K}_4\text{Fe}(\text{CN})_6$ , ml.	Back-titrn. : 0.01M-In, ml.	Ratio In/ $\text{K}_4\text{Fe}(\text{CN})_6$
5	5.0, 6.0	1.24, 2.52	1.25, 1.25	1	1.5, 1.0	0.90, 0.25	1.27, 1.25
10	10.0, 15.0	2.50, 8.72	1.25, 1.25	2	2.0, 3.0	0.48, 1.72	1.24, 1.24
15	15.0, 15.0	3.77, 3.73	1.25, 1.25	4	4.0, 6.0	1.00, 3.47	1.25, 1.25
20	20.0, 25.0	5.10, 11.30	1.26, 1.25	5	5.0, 5.5	1.26, 1.92	1.25, 1.26
				10	10.0, 12.0	2.52, 4.97	1.25, 1.25

#### EXPERIMENTAL.

*Solutions required.*—*Cadmium*, 0.05M., 0.01M. The solutions were prepared by dissolving "AnalaR" cadmium sulphate in distilled water, and standardised by gravimetric determination of the cadmium with 8-hydroxyquinoline.

*Calcium*, 0.05M., 0.01M. These were prepared by dissolving "AnalaR" calcium carbonate in 2N-hydrochloric acid and neutralising them with 1N-sodium hydroxide; they were standardised by gravimetric determination of the calcium as oxalate.

*Indium*, 0.05M., 0.01M. Pure indium metal was dissolved in 11N-hydrochloric acid, the solution evaporated to dryness, and the resulting chloride dissolved in distilled water.

*Potassium ferrocyanide*, 0.05M., 0.01M. "AnalaR" Potassium ferrocyanide trihydrate was dissolved in distilled water containing 0.2 g. of sodium carbonate per litre. The solutions were standardised by titration with a standard zinc solution, 3 : 3'-dimethylnaphthidine being used as indicator.

*Potassium ferricyanide*. 1% Solution was prepared fresh each day and kept in a dark bottle.

*Ammonium sulphate*. 10% Solution.

*Indicator : 3 : 3'-dimethylnaphthidine*. Prepared by dissolving, with warming, 1 g. of the compound in 100 ml. of glacial acetic acid.

*Titration of Cadmium.*—10 ml. of 10% ammonium sulphate were added to 1—10 ml. of neutral cadmium solution and the volume adjusted to 40 ml. with distilled water. Two drops of 1% potassium

ferricyanide and 2 drops of indicator were added, and the solution was titrated with potassium ferrocyanide solution until the colour changed from red-violet to white.

*Titration of Calcium.*—35 Ml. of ethyl alcohol were added to 1—5 ml. of neutral calcium solution, and the volume adjusted to 40 ml. with distilled water. Further procedure was as above, but the solution was titrated moderately rapidly until a slight fading of the indicator occurred, and then dropwise to a permanent change from pink to pale yellow.

*Titration of Indium.*—Sufficient distilled water was added to 1—20 ml. of neutral indium solution to give a volume of 40 ml. and 4 drops of potassium ferricyanide solution and 2 drops of indicator were added. Potassium ferrocyanide solution was added in excess, and the solution back-titrated with a standard indium solution until its colour changed from grey-white to pink-violet.

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY,  
EDGBASTON, BIRMINGHAM, 15.

[Received, July 16th, 1951.]

---