

# BRUCINE SULPHATE AS AN INTERNAL INDICATOR IN TITRATIONS WITH STANDARD DICHROMATE SOLUTION.\*

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THE elegant method of determining iron volumetrically with permanganate cannot be employed in the presence of hydrochloric acid except after the addition of manganous sulphate and phosphoric acid. This procedure, however, has not found general favour and in spite of the disadvantage in the use of an external indicator, dichromate method has more or less been universally adopted. The discovery of diphenylamine as an internal indicator in such titrations (Knop, 1924) was therefore a great advance in this field. This substance gives an intense blue colour when treated with a drop of 0.1 normal solution of potassium dichromate in hydrochloric acid or sulphuric acid containing trivalent iron. The addition of excess of ferrous salt decolourises the indicator so that back titration is possible. Recently Phenanthroline has been studied in detail as an indicator in oxidimetry (Walden and Edmonds, 1935) and has been found to be very satisfactory. But the difficulty with which it is synthesised is for the present against its widespread use

Though with a strict adherence to the optimum conditions (Sarver, 1927) one may obtain satisfactory results with diphenylamine, there are certain drawbacks in its use. In the presence of the green colour of the chromic salt and the yellow of the ferric salts the end point frequently ceases to be sharp and considerable difficulty is experienced in judging it even after the addition of phosphoric acid. An indicator giving a more easily detectable colour, which is not masked by the chromic or ferric salts, should be more valuable and one such has been found in Brucine. 1 c.c. of a 1 per cent.

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\* After our work described in this paper had been completed, it was realised that the use of Brucine as an internal indicator had been indicated by Seikichi Miyagi (*J. Soc. Chem. Ind. Japan* 36, suppl. binding 1933, 146-47). Since, however, the Japanese author had not examined the scope of the method in detail, we thought it would be useful to publish our results.  
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solution of brucine in 100 c.c. of water containing sulphuric acid is coloured a distinct red with one drop of N/100 dichromate solution: this red colour is quite easily visible in the presence of chromic and ferric salts and there is no need to add phosphoric acid as in the case of diphenylamine indicator in order to improve the sharpness of the end point.

The indicator solution is prepared by dissolving one gram of brucine in 100 c.c. of 3 N sulphuric acid and preserved in a stoppered amber coloured bottle. The colourless solution turns pale brown on standing without however losing its usefulness. It is not desirable, however, to prepare more than 100 c.c. at a time. It is further noticed that the indicator functions best only after standing for a few hours after it has been made. Its use in the different methods employing dichromate titrations is illustrated below. 10 drops of the brucine solution are used as indicator. When titrating ferrous salts against dichromate, near the end point—within 3 drops of it—the solution changes to a dirty green and with the first excess drop of dichromate the solution becomes red. The faintest trace of red is easily detected in the presence of the green chromic salt. It is necessary that the acid strength of the solutions is not allowed to fall below 2 normal, though above that it may be allowed to vary within wide limits. Back titration using this indicator is not quite sharp probably due to the oxidation product not undergoing reduction easily.

TABLE I.

Wt. of Ferrous am. sulphate in grams	Vol. of 0.1015 N $\text{KMnO}_4$ in c.c. (a)	Vol. of 0.1 N Dichromate in c.c. (b)	Fe calculated in grams	
			From (a)	From (b)
0.2025	5.05	5.15	0.0286	0.0288
0.4104	10.05	10.20	0.0570	0.0570
0.6060	15.15	15.35	0.0858	0.0857
0.9015	22.60	23.00	0.1280	0.1284
1.2500	31.25	31.70	0.1771	0.1770
1.8050	45.25	46.00	0.2564	0.2569

Table I compares the results obtained by titrating varying amounts of ferrous ammonium sulphate against standard permanganate on the one hand, and dichromate using brucine sulphate as internal indicator on the other.

The agreement between the two methods is quite close. The colour due to the ferric iron does not affect the sharpness of the end point and this

is further confirmed by adding known large quantities of ferric chloride to the ferrous salt solution that has to be titrated.

TABLE II.

*Concentration of dichromate solution 0.1 N.*

*Concentration of ferric chloride 0.2 N.*

*Concentration of ferrous ammonium sulphate 0.1 N.*

Vol. of FeCl <sub>3</sub> added in c.c.	Vol. of Ferrous am. sulphate in c.c.	Vol. of water in c.c.	Vol. of 0.1 N dichromate required in c.c.
10.0	25.0	70	25.00
20.0	25.0	60	25.05
40.0	25.0	40	25.05
80.0	25.0	..	25.05

The indicator is therefore useful in the estimation of chrome-iron alloys and ores in which the ferric iron is present in large quantities and has been utilised by us for the analysis of the ore.

Mercuric chloride, mercurous chloride and stannic chloride do not affect the end point and this was settled by analysing a ferric chloride solution in two ways :— (1) the iron was precipitated as ferric hydroxide, filtered, washed and dissolved in 1 : 1 sulphuric acid and after reduction with arsenic-free zinc titrated against standard permanganate ; (2) the solution was reduced with stannous chloride, excess of the stannous salt oxidised with mercuric chloride and then titrated against potassium dichromate using brucine sulphate as indicator. The comparative results are given in Table III and they are very concordant.

TABLE III.

Vol. of FeCl <sub>3</sub> in c.c.	0.1015 N permanganate in c.c. (1)	0.1 N dichromate in c.c. (2)	Amount of iron present in grams	
			From (1)	From (2)
10.0	16.95	17.30	0.0961	0.0966
10.0	17.00	17.25	0.0963	0.0963
25.0	42.60	43.25	0.2415	0.2414
25.0	42.45	43.20	0.2410	0.2417

The above fact was further proved by analysis of samples of Kahlbaum's purest specimen of iron wire. The wire was converted into ferric chloride and the iron estimated as above using dichromate and brucine.

TABLE IV.

Wt. of iron wire in gms.	0.1143	0.1365	0.1893	0.2632
0.1 N $K_2Cr_2O_7$ in c.c. ..	20.50	24.40	33.90	47.10
Fe% .. ..	100.1	99.82	100.0	99.90

Titration of ferrous iron in the presence of hydrochloric acid with permanganate is possible when diphenylamine is used as indicator and brucine can be employed for the same purpose with equal advantage. Chlorine that may be liberated from hydrochloric acid affects the indicator just as any other oxidising agent and acts as so much permanganate. Table V records data obtained to illustrate this aspect of the use of brucine.

TABLE V

*Ferric chloride solution reduced with stannous chloride etc., and titrated against 0.1015N potassium permanganate.*

Vol. of Ferric chloride soln. in c.c.	Vol. of Pot. permanganate in c.c.	Amount of iron	
		Found in gm.	Taken in gm.
10.0	16.90	0.0958	0.0965
10.0	17.00	0.0963	0.0965
25.0	42.55	0.2412	0.2415
25.0	42.50	0.2409	0.2415

*Application to soil analysis.*—As a rapid approximate method for the estimation of soil organic matter Schöllenger (1927) recommends the oxidation of the organic matter with excess of chromic acid and estimation of the excess of the oxidant by titration with ferrous ammonium sulphate using diphenylamine as indicator. It is now found that brucine can be used for the purpose with advantage. After the oxidation is over, the chromic acid solution is diluted, a known excess of ferrous ammonium sulphate solution is added and the excess of the ferrous salt titrated against standard dichromate. Direct titration of the chromic acid with ferrous sulphate is not possible with

brucine as indicator and is not very advisable even with diphenylamine since undesirable oxidation products are formed. Concordant results are obtained with brucine as shown below :—

TABLE VI.

	Wt. of soil sample	Per cent. C-content	Deviation from the Mean
A. Low Grade	0.5005	2.50	-0.03
	0.3080	2.48	-0.05
	0.4254	2.60	0.07
	Mean	2.53	
B. High Grade	0.3412	5.06	0.05
	0.4215	5.02	-0.01
	0.3915	4.96	-0.05
	Mean	5.01	

*Summary.*

Brucine sulphate has been shown to be a good internal indicator for titrations with dichromate and in certain respects superior to diphenylamine. The colour change from green to bright red at the end point is much more pronounced than the change from green to blue in the case of diphenylamine.

It has been shown that in titrations with potassium permanganate solutions, the disturbing effects due to the presence of hydrochloric acid may be obviated by using brucine as an internal indicator. The presence of ferric iron has not been found to interfere with the sharpness of the end point.

The use of this indicator in the analysis of chromium ores and in the estimation of organic matter in soils by the Schöllenger method has been indicated.

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- 4 Walden and Edmonds, *Chemical Reviews*, 1935, **16**, 81.