116. *Substituted Benzidines and Related Compounds as Reagents in Analytical Chemistry. Part III.* 3-*Methylbenzidine and* 3 : 3′-*Diethylbenzidine as Indicators in Argentometry.*

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3-Methylbenzidine and 3 : 3′-diethylbenzidine are recommended in place of benzidine as indicators for the titration of silver solutions with bromide or iodide. The colour changes at the end-point are more satisfactory than those given by benzidine, and considerably sharper than those given by the conventional adsorption indicators; moreover, the new indicators can be used in more dilute solution.

Benzidine has been recommended as indicator in the titration of silver solutions with bromide (Burriel, *Anal. Soc. Fís. Quím.*, 1935, **33**, 692) and with iodide (Sierra and Burriel, *ibid.*, 1932, **30**, 366). The end-points are claimed to be superior to those obtained when the conventional adsorption indicators are used, and more dilute solutions may be titrated. Since, in general, our own experience confirmed these observations, we have examined the behaviour of the series of amines described in the preceding papers when substituted for benzidine in this reaction. In the original work benzidine acetate and benzidine sulphate were used as indicators in conjunction with copper acetate for titrations with bromide, and with copper nitrate for titrations with iodide, the colour change at the end-point being from light yellow to green and from greenish-yellow to greyish-blue, respectively.

The reaction is claimed to proceed as follows (Bnz = benzidine; X = halogen):

$$2KX + 2Cu(NO_3)_2 + H_2SO_4,Bnz \longrightarrow 2CuBnzX_2 + K_2SO_4 + 2HNO_3$$

and also by the formation of free halogen

$$2KX + 2Cu(NO_3)_2 \longrightarrow CuX_2 + 2KNO_3;\ 2CuX_2 \longrightarrow Cu_2X_2 + X_2$$

which oxidises benzidine to benzidine-blue. Both the copper benzidine complex and the benzidine-blue are adsorbed by the silver halide at the end-point.

Two substituted benzidines, 3-methyl- and 3 : 3′-diethyl-benzidine, were found to give end-points as sharp as those obtained with benzidine, and the colour changes were easier to observe. The end-points were sharp to within 1 drop and the results were comparable with those obtained when benzidine was used as indicator. Titrations were carried out with 0·1N-, 0·01N-, and 0·001N-solutions. Typical results are listed in the table.

0·1N-$AgNO_3$, taken, ml.	20	20	15	15	10	10	5	5
0·1N-KBr required, ml.	19·96	19·99	—	15·02	10·00	10·00	5·00	4·98
0·1N-KI required, ml.	19·98	20·00	15·00	14·96	9·98	9·99	4·98	5·00
0·01N-$AgNO_3$ taken, ml.	20	20	10	10				
0·01N-KBr required, ml.	19·96	19·98	10·00	9·96				
0·01N-KI required, ml.	20·00	19·96	9·96	9·98				
0·001N-$AgNO_3$ taken, ml. ...	20	20	10	10				
0·001N-KBr required, ml. ...	20·00	19·94	19·98	10·00				
0·001N-KI required, ml.	19·96	19·98	9·98	9·99				

The reverse titration could not be carried out, but when a small excess (1 or 2 drops) of bromide or iodide was added, this excess could be back-titrated with standard silver nitrate. When a larger excess of bromide or iodide was added an end-point could still be obtained on back-titration, but the colour changes were not so well-defined.

The indicators function best in neutral solution. When the hydrogen-ion concentration exceeds that corresponding to 3 ml. of 1N-acetic acid or 2 ml. of 0·1N-nitric acid in an initial volume of 20 ml. of solution, poor end-points are obtained.

Chlorides cannot be determined in this way.

Experimental.—Indicator solutions. A suspension of 0·5 g. of the sulphate of 3-methylbenzidine or 3 : 3′-diethylbenzidine in 100 ml. of a saturated solution of sodium sulphate was used.

Titration procedure. Different amounts of silver nitrate solution (as in table) were measured into a conical flask, and 1 ml. of 5% aqueous copper acetate solution and 10 drops of indicator suspension were added. The solutions were then titrated with potassium iodide or potassium bromide with continual shaking until the colour changed from yellow to blue-green.

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