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FAST SULPHON BLACK F AS AN INDICATOR FOR THE EDTA TITRATION OF COPPER

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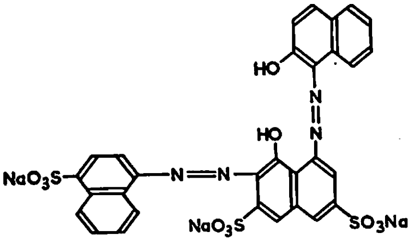
Copper (II) can be titrated with EDTA using murexide, catechol violet or PAN as indicator.[1] None of these is specific for copper; for example calcium and nickel form coloured products with murexide, and the majority of other divalent cations give coloured products with catechol violet and with PAN. The latter is perhaps the most selective of the three, but the reaction appears to be sluggish and is less preferable than the other two. In the course of a systematic study of various EDTA indicators, we have found that the *bis*-azo dyestuff Fast Sulphon Black F (B.C.I. No. 306) is virtually specific in its colour reaction with copper. In the presence of ammonia this dye forms a crimson colour with Cu (II) ions; the addition of excess EDTA changes the colour back to green. In moderately strong Cu (II) solution the blue colour of the cuprammonium ion causes the colour change to be from pale blue to bright green. If a large amount of indicator is used, a red to green end-point can be obtained, but it occurs too soon and is less distinct. This indicator is virtually specific for Cu (II); nickel is the only other ion of the many we have examined which forms a coloured product, but the nickel complex cannot be used satisfactorily as an indicator. Thus, copper is the only metal which can be titrated directly using this indicator.



Fast Sulphon Black F

The presence of ammonia is essential for colour formation. This suggests that the constitution of the complex is such that two ammonium molecules are probably co-ordinated on to the copper atom. Pyridine also gives a red colour but it reacts too sluggishly to be used in place of ammonia. Other buffering agents of equivalent pH, *viz.* borate, hydroxide-tartrate, diethylamine, etc., do not promote colour formation. In all cases, the addition of a few drops of ammonia causes instant formation of the red copper complex, although titration of the copper under these conditions is not always practicable.

The results of the titration of varying amounts of 0·02M copper chloride solution with 0·02M EDTA are shown in the following Table. Each result shown represents the mean of 10 titrations using the prescribed method. In no case did the result of any titration differ from the mean by more than 0·04 ml.

Table

0·02M Cu^{2+} *taken (ml.)*	*Found (mean of* 10)	*Standard Deviation*	*Molarity (calc.)*
5·00	5·01	0·023	0·0200
10·00	10·02	0·024	0·0200
15·00	15·00	0·031	0·0200
20·00	20·00	0·026	0·0200
25·00	25·00	0·039	0·0200

Interference is found from other metal ions which form soluble complexes with EDTA at the pH at which the copper (II) titration is carried out. Most of these metals can themselves be determined simply by buffering to the correct pH, adding a known amount of copper (*ca.* 50% as much as the cation concerned) and indicator, and titrating in the usual way. If insufficient copper is added, indistinct and premature end-points may occur. In this way, it is possible to carry out accurate titration of metals such as cadmium, calcium, barium, lead, nickel, and zinc. Poor results were obtained with magnesium possibly because of the pH requirements. (pH 10—11·5)

This indicator is recommended on the grounds of the sharpness of the end-point and because of the lack of serious interference by trace metals. The experimental procedure adopted is as follows:

Solutions required

0.02M EDTA;
0.02M Cupric chloride;
Ammonia solution (*S.G.* 0.88);
Fast Sulphon Black F.—0.5% in water.

A suitable amount of copper solution was transferred to a 250 ml. conical flask, and diluted with an equal volume of distilled water. To each 10 ml. of dilute solution, 1 ml. of concentrated ammonia was added and 2 drops of the indicator. The solution was titrated with 0.02M EDTA to the pale blue to bright green end-point.

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Reference

[1] Barnard, A. J., Broad, W. C. & Flaschka, H., *Chemist Analyst*, 1956, **45**, 86, 111; 1957, **46**, 18, 46, 76

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