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INDICATOR CORRECTIONS FOR DIPHENYLAMINE, DIPHENYLBENZIDINE AND DIPHENYLAMINE SULFONIC ACID

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Introduction

The reaction mechanisms of the oxidation of diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid have been discussed in previous papers,[1] and it may be predicted from these that in the titration of reducing agents with potassium dichromate, diphenylbenzidine will require a negligible correction, whereas diphenylamine or diphenylamine sulfonic acid ought to consume an equivalent amount of reagent for their oxidation to the diphenylbenzidine state. In the titration of oxidizing agents with ferrous iron, however, it is hard to predict the size of the corrections, because of the instability of the colored holoquinoid compounds. Therefore an extensive study has been made of the analytical conditions and indicator corrections necessary for diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid in the various titrations.

I. Indicator Solutions.—Each indicator was made up so as to be 0.005 molar (1.69 g. of diphenylamine per liter of concentrated sulfuric acid; 1.68 g. of diphenylbenzidine per liter of nine parts glacial acetic acid and one part concentrated sulfuric acid; 3.17 g. of anhydrous barium salt of diphenylamine sulfonic acid per liter of water), and to require theoretically an equal volume of 0.01 *N* oxidizing or reducing solution for each stage of the oxidation of the indicator.

II. Standard Solutions.—The dichromate solution was prepared by dissolving a given weight of pure potassium dichromate in water, and making up to a known volume. The ferrous and vanadate solutions were then standardized potentiometrically.

III. Titration of Ferrous Iron with Potassium Dichromate. 1. Recommended Conditions.—The solutions should be about 1.0 *N* with sulfuric or hydrochloric acid (the former being somewhat preferable), but they may vary between 0.5–2.0 *N* when diphenylamine or diphenylbenzidine is used as indicator, or between 0.25–3.0 *N* when diphenylamine sulfonic acid is used. About 10 cc. of 25% phosphoric acid should be present for each 50 cc. of volume, but considerable variation is permissible. Mercuric chloride renders color development slower with diphenylamine or diphenylbenzidine, but does not otherwise affect the accuracy of the titration; it has no appreciable effect upon the behavior of diphenylamine sul-

[1] I. M. Kolthoff and L. A. Sarver, THIS JOURNAL, **52**, 4179 (1930); L. A. Sarver and I. M. Kolthoff, *ibid.*, **53**, 2902 (1931).

fonic acid. In those cases where color development is slow, the oxidation of the indicator can be speeded up by warming to 50°, but the colors are then less permanent; diphenylbenzidine is generally less satisfactory than the other two for titrations of ferrous iron by dichromate, on account of the slowness of color development. No unnecessary excess of stannous chloride should be used in the reduction of the iron, because of the large amount of mercurous chloride precipitate obtained later. Stannic and manganous salts have no effect upon any of the three indicators, but only diphenylamine sulfonic acid can be used in presence of tungstate. Titrations can be made with 0.1, 0.01 or 0.001 *N* dichromate, but diphenylbenzidine is not recommended for the weaker solutions. Diphenylamine sulfonic acid is recommended for the micro-titration of ferrous iron, it being possible to determine 0.5 mg. of iron in a small volume within an accuracy of 1%. Especially when titrating with the weaker solutions, the volumes should not greatly exceed 50 cc., although they may be 100–250 cc. for 0.1 *N* dichromate.

2. Recommended Amounts of Indicators.—For titrations with 0.1 *N* dichromate in 100–250 cc. volumes, 5–6 drops of 0.005 molar indicator (7–10 drops of 0.1% diphenylamine or diphenylbenzidine or of 0.2% diphenylamine sulfonic acid barium salt) should be used. With 0.01 or 0.001 *N* dichromate in 10–50 cc. volumes, 0.02–0.05 cc. of 0.005 molar diphenylamine or diphenylamine sulfonic acid (0.03–0.06 cc. of 0.1% diphenylamine or 0.2% diphenylamine sulfonic acid barium salt) will give sharp distinct color changes.

3. Indicator Corrections.—Indicator corrections for titrations with 0.01 and 0.001 *N* dichromate solutions, respectively, are given in Table I. It is seen that the excess of dichromate required for obtaining an end-point increases with increasing amounts of indicator; with diphenylamine, the corrections were found to be approximately the theoretical for amounts up to 0.3 cc. of 0.005 molar indicator, and 0.1 cc. of 0.01 *N* dichromate (or 1.0 cc. of 0.001 *N* dichromate) should be deducted for each 0.1 cc. of

TABLE I

INDICATOR CORRECTIONS FOR TITRATIONS OF FERROUS IRON WITH 0.01 OR 0.001 *N* POTASSIUM DICHROMATE SOLUTION

For each titration, 10 cc. of 0.01 or 0.001 *N* ferrous solution was added to a mixture of 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc. of water and the stated volume of indicator.

Volume of 0.005 *M* indicator, cc.	Diphenylamine Excess of $K_2Cr_2O_7$ required, cc. 0.01 *N*	0.001 *N*	Diphenylamine sulfonic acid Excess of $K_2Cr_2O_7$ required, cc. 0.01 *N*	0.001 *N*
0.02	0.01	0.21	0.02	0.21
.04	.04	.41	.05	.44
.10	.10	.95	.18	.93
.20	.21	1.90	.34	1.85
.30	.39	..	.51	3.48
.50	.63	..	0.75–0.90	..

indicator used (0.06 cc. and 0.6 cc., respectively, for each 0.1 cc. of 0.1% diphenylamine). With larger amounts of indicator, the presence of much diphenylbenzidine green interferes with the observation of the color. With diphenylamine sulfonic acid also, the corrections (expressed in terms of 0.01 *N* oxidizing solution) were found to be equal to the volume of 0.005 molar indicator (0.06 cc. of 0.01 *N* solution for each 0.1 cc. of 0.2% diphenylamine sulfonic acid barium salt) when less than 0.3 cc. was used and the titration made with 0.001 *N* dichromate solution; but when the titrations were made with 0.01 *N* dichromate solution, the corrections were somewhat larger than the theoretical.

IV. Titration of Dichromate or Vanadate Solutions with Ferrous Iron.—The same considerations as to titration volume, quantity of indicator and concentrations of phosphoric acid and sulfuric or hydrochloric acid, apply to the titration of 0.01 *N* dichromate or vanadate by 0.01 *N* ferrous iron. The presence of sodium acetate in the vanadate titration, as recommended by Willard and Young,[2] does not seem to be necessary, although the neutralization of the strong mineral acid does take away a disturbing color when much ferric iron is present. The violet color develops very slowly in acid dichromate solutions, especially when diphenylamine sulfonic acid is used as indicator, but a brilliant color appears instantly when the titration with ferrous iron is begun. In an acid vanadate solution the color develops rapidly without the addition of ferrous iron, so the titration can be started almost immediately after the addition of any of the three indicators.

TABLE II

INDICATOR CORRECTIONS FOR TITRATIONS OF DICHROMATE OR VANADATE SOLUTIONS WITH 0.01 *N* FERROUS IRON SOLUTION

For each titration, 10 cc. of 0.01 *N* dichromate or vanadate solution was added to a mixture of 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc. of water and the stated volume of indicator; the whole was then titrated at once with 0.01 *N* ferrous solution. The volumes given below should be added to the volume of 0.01 *N* ferrous solution used in any given titration.

Volume of 0.005 *M* indicator, cc.	Diphenylamine		Diphenylbenzidine		Diphenylamine sulfonic acid	
	Dichromate, cc.	Vanadate, cc.	Dichromate, cc.	Vanadate, cc.	Dichromate, cc.	Vanadate, cc.
0.02	0.04	0.03	0.02	0.03	0.05	0.03
.04	..	..	.04	.05	.13	.12
.10	.24	.20	.10	.11	.31	.30
.20	..	.40	.17	.20	.58	.60
.30	.63	.63	.24	.29	.95	.95
.50	..	..	.36	..	..	..

From the data in Table II it is seen that the indicator corrections are approximately the same in the dichromate and the vanadate titrations. If the titration is started immediately after the addition of the indicator

[2] H. H. Willard and Philena Young, *Ind. Eng. Chem.*, **20**, 764 (1928).

0.1 cc. should be added to the volume of 0.01 N ferrous solution required for each 0.1 cc. of 0.005 M diphenylbenzidine (0.06 cc. for each 0.1 cc. of 0.1% diphenylbenzidine), 0.2 cc. for each 0.1 cc. of 0.005 M diphenylamine (0.12 cc. for each 0.1 cc. of 0.1% diphenylamine) and 0.3 cc. for each 0.1 cc. of 0.005 M diphenylamine sulfonic acid (0.18 cc. for each 0.1 cc. of 0.2% diphenylamine sulfonic acid barium salt). The correction is smaller for diphenylbenzidine than for diphenylamine, as could be expected. Diphenylamine sulfonic acid has the largest correction, but it is still recommended because it gives a sharp, brilliant color change, and can be used in the presence of tungstate. If the titration is not started immediately after the addition of the indicator, the corrections will be larger, on account of the decomposition of the holoquinoid compounds. This increase in the correction with time is negligible in the case of diphenylbenzidine when the titration is completed within fifteen minutes after the addition of the indicator, but it is appreciable in the case of diphenylamine sulfonic acid. For example, when a mixture of 10 cc. of 0.01 N vanadate solution, 10 cc. of 25% phosphoric acid, 1.2 cc. of concentrated sulfuric acid, 15 cc. of water and 0.2 cc. of 0.005 M diphenylamine sulfonic acid, was titrated with 0.01 N ferrous solution as quickly as possible, the correction was 0.58 cc. of 0.01 N solution; but after five, ten, fifteen and thirty minutes' standing, the corrections were 0.62, 0.68, 0.74 and 0.76 cc., respectively.

Summary

Analytical conditions (acidity, volume, amount of indicator, etc.) and indicator corrections have been given for the titration of 0.1, 0.01 and 0.001 N ferrous solutions with 0.1, 0.01 and 0.001 N potassium dichromate solutions, respectively, as well as similar information on the titration of 0.01 N dichromate or vanadate solutions with 0.01 N ferrous iron solution, using diphenylamine, diphenylbenzidine and diphenylamine sulfonic acid as indicators. Diphenylamine sulfonic acid is recommended because of its rapid brilliant completely reversible color changes, and its usefulness in the presence of tungstate.

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