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DIPHENYLAMINE AS INDICATOR IN THE TITRATION OF IRON WITH DICHROMATE SOLUTION

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At the present time there is no suitable internal indicator for Penny's[1] titration of iron with potassium dichromate. Brandt[2a] proposed diphenylcarbazide, which gives a red color in the presence of the ferric salts formed in the titration, but is colorless in the presence of an excess of dichromate, and his conclusions were sustained by Barnebey and Wilson.[2b] The results obtained by this method depend on the conditions of the analysis, the amount of indicator used, and very little upon the amount of iron taken.

While the influence of oxidizing agents on solutions containing very small amounts of diphenylamine sulfate in the presence of concd. sulfuric acid was being studied, some reactions were observed which differed from the known reactions of diphenylamine. A dilute aqueous solution of diphenylamine sulfate acidified with hydrochloric or sulfuric acid and containing ferric salts gives the familiar blue color only after some time (influence of air or oxygen?), but an intense blue color results immediately when one drop of 0.1 *N* potassium dichromate solution is added. When ferrous salts are also present no coloration is produced until these are oxidized to the ferric state, the first excess drop of bichromate solution then forming an intense violet-blue coloration which completely masks the color of the chromic salts formed by titration. The addition of a solution of ferrous salt causes the solution to become colorless, so that back-titration is possible. In the absence of iron salts no coloration is

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[1] Penny, *Chem. Gaz.*, **8**, 330 (1850).

[2] (a) Brandt, *Z. anal. Chem.*, **45**, 95 (1906); **53**, 1, 729 (1914). (b) Barnebey and Wilson, THIS JOURNAL, **35**, 156 (1913).

produced by bichromate, the reaction thus differing from that which takes place in the presence of concd. sulfuric acid.

The above reactions can be explained on the basis of the work of Kehrmann and Micewicz,[3] according to which there is formed during the oxidation of diphenylamine by ferric salts a green semi-quinoid salt of diphenylbenzidine, which is converted by chromic acid into the dark blue quinoid salt.

Preliminary experiments showed that the end-point was sufficiently distinct if the amount of iron taken corresponded to only a few cubic centimeters of 0.1 *N* potassium dichromate solution. Greater quantities of iron caused the troublesome yellow color of ferric chloride to interfere with the sharpness of the end-point. This was avoided by the use of a mixture of sulfuric acid and phosphoric acid, which gave a sharp end-point with amounts of iron corresponding to almost 50 cc. of 0.1 *N* dichromate solution.

Solutions Required in Titration

1. 0.1 *N* Potassium dichromate solution.
2. A mixture of sulfuric acid and phosphoric acid. This is prepared as follows: 150 cc. of sulfuric acid (d., 1.84) is mixed with 150 cc. of phosphoric acid (d., 1.7) and the mixture diluted with water to 1000 cc.; 15 cc. of this solution is used in titration.
3. Diphenylamine solution, consisting of 1 g. of diphenylamine dissolved in 100 cc. of concd. sulfuric acid. Three drops of the solution are used as indicator. The solution becomes brown after some time without, however, losing its usefulness, as a very brown solution proved to be good eight months after it had been prepared.

Titration of Ferrous Salts

The ferrous salt solution is acidified with 20 cc. of 1:1 hydrochloric acid or 20–25 cc. of sulfuric acid (1:4), and 15 cc. of phosphoric acid mixture and 3 drops of indicator solution are added; the solution is then diluted with water to 150–200 cc. and titrated with 0.1 *N* dichromate solution. Near the end-point the green color of the solution deepens to blue-green or, in the presence of larger amounts of iron, almost to grayish-blue. At this stage the dichromate is added in drops. The end-point is taken as the point when a drop causes an intense violet-blue coloration that remains unchanged on the further addition of dichromate. A titration in which 20–30 cc. of dichromate solution is reduced gives the sharpest end-point. The correction 0.05 cc. for the oxidation of diphenylamine must be subtracted from the volume of the dichromate added.

The acidity of the solution may vary between rather wide limits, no difference in the results being observed between a solution containing 6 cc. of 1:1 hydrochloric acid and one containing 40 cc. of hydrochloric acid in 200 cc. of solution. It is advisable, however, to maintain the acidity mentioned above.

Table I compares the results obtained on titrating approximately 0.1 *N* ferrous sulfate with 0.1 *N* dichromate and with 0.1 *N* potassium permanganate solutions, and the results of titrating approximately 0.01 *N* ferrous sulfate solution; the latter was standardized with 0.1 *N* permanganate solution, 200 cc. being oxidized by 20.31 cc. of the latter solution.

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[3] Kehrmann and Micewicz, *Ber.*, **45,** 2641 (1912).

Table I

Titration of Ferrous Salt Solutions

0.1 *N* Fe^{++} soln. Cc.	0.1 *N* $KMnO_4$ Cc. req.	0.1 *N* $K_2Cr_2O_7$ Cc. req.	0.01 *N* Fe soln. Cc.	0.01 *N* $K_2Cr_2O_7$ Calc. Cc.	Req. Cc.
50	49.84	49.82	50	50.76	50.79
40	39.86	39.88	40	40.61	40.65
30	29.88	29.87	30	30.46	30.55
20	19.94	19.93	20	20.31	20.44
10	9.98	9.96	10	10.15	10.38

The influence of copper and arsenic on the results of titration is shown in Table II. Copper lowers the results, for in the presence of cupric salts the rate of oxidation of ferrous salts by the oxygen of the air is greatly increased, but quantities of copper less than 1 mg. have no effect. Trivalent arsenic, however, raises the results, since it is oxidized to the pentavalent state by dichromate solution; this reaction is not quantitative but its velocity is proportional to the quantity of iron present.

Table II

Influence of Copper and Trivalent Arsenic on Titration

20 cc. of ferrous sulfate solution used in the first five experiments; 40 cc. in the last five

Cu Mg.	0.1 *N* $K_2Cr_2O_7$ Cc.	Diff. Cc.	As Mg.	0.1 *N* $K_2Cr_2O_7$ Cc.	Diff. Cc.
..	19.94	....	...	19.94	....
10.0	19.87	−0.07	0.5	19.96	+0.02
20.0	19.82	− .12	1.0	20.04	+ .10
40.0	19.73	− .21	5.0	20.44	+ .50
50.0	19.63	− .31	10.0	20.86	+ .92
..	39.85	....	...	39.85	....
10.0	39.68	−0.17	0.5	39.89	+0.04
20.0	39.61	− .24	1.0	40.00	+ .15
40.0	39.63	− .22	5.0	40.45	+ .60
50.0	39.59	− .26	10.0	40.86	+1.01

Experiments to determine the influence of greater amounts of ferric salts on the titration results and on the sharpness of the color change showed that ferric iron, in amounts up to 1 g., gave a reliable color change when the latter was observed with a daylight background; the results differed only within the limits of experimental error. Twenty cc. of approximately 0.1 *N* ferrous sulfate solution alone required 19.20 cc. of 0.1 *N* potassium dichromate solution; but when 0.280, 0.560, 0.840 and 1.121 g. of ferric iron was added, it required 19.25, 19.25, 19.20 and 19.30 cc. of dichromate solution, respectively. It was, therefore, possible to apply this method to the determination of chromium in chromium steel. A sample of chromium steel of known chromiun content was dissolved in 1 : 1 sulfuric acid and the solution oxidized by means of ammonium persulfate; the precipitate of basic manganese hydroxide, $MnO(OH)_2$, was filtered off, and the chromic acid formed was determined by adding an excess of approximately 0.1 *N* ferrous sulfate solution and titrating back with dichromate solution.

TABLE III

DETERMINATION OF CHROMIUM IN CHROMIUM STEEL

Sample	1	2	3	4	5
Cr present, %	0.15	0.26	0.63	1.04	2.42
Cr found, %	0.18	0.27	0.65	1.11	2.51

Zinc, aluminum, manganese, nickel, cobalt and chromium have been found to have no effect on the results of titration, except that rather great amounts of manganese salts dull the violet color. The colors of chromium, nickel and cobalt salt solutions do not interfere, and the method is particularly advantageous for the titration of ferrous salts in the presence of these elements. The titration with permanganate would be impossible in such cases, owing to the light pink end-point which would be masked by the color of the solution; but the intense blue color of diphenylamine prevails over the original color of the solution.

Organic substances which are, in general, more readily oxidized by permanganate than by dichromate do not interfere in titration with the latter.

Since the violet end-color is caused by a change in structure of the diphenylbenzidine molecule, back-titration is possible. If in the titration an excess of dichromate has been added it may be titrated back with a ferrous salt solution of known strength until the violet color is replaced by the original green color; or an excess of ferrous salt solution may be added at the beginning and the titration continued to the formation of the violet color. In the latter case the volume of dichromate solution corresponding to the added ferrous salt solution must be carefully determined.

Titration of Ferric Salts Reduced with Stannous Chloride

Although the titration of simple ferrous salts may be effected with equal precision using either the permanganate or the dichromate method, it is well known that in the case of ferric salt solutions which have been reduced by stannous chloride, the permanganate method, commonly called the Zimmermann-Reinhardt method, is empirical, and gives results depending on many factors difficult to control. In Penny's method, however, hydrochloric acid does not interfere with the titration and it was, therefore, possible to apply to this analysis the dichromate method, employing diphenylamine as indicator, obtaining a procedure combining rapidity, smoothness of reduction, and exactness and avoiding the faults of the Zimmermann-Reinhardt method.

The influence of mercuric chloride, mercurous chloride and stannic chloride on the color of the indicator was tested as follows. To a ferric salt solution reduced by stannous chloride were added 15 cc. of the phosphoric acid mixture and 3 drops of diphenylamine solution. The solution was then made up to 150–200 cc. and titrated with dichromate solution. The color changes were found to be somewhat different from those in the titration of ferrous salts alone; at the moment when the ferrous salt was completely oxidized, the dark green color of the liquid changed suddenly to a blue-black color which was quite permanent. The diphenylamine method is therefore to be preferred to the permanganate method, in which the rose color quickly vanishes due to the action of mercurous chloride. The presence of chloride ion and mercurous chloride has an infinitesimal influence on the results of titration; in a great number of titrations the error due to these substances was found to average 0.1% of the result.

In order to test the accuracy of the method when applied to ferric salt solutions reduced by stannous chloride, weighed quantities of two different samples of ferric oxide of the highest commercial quality used as standard reagents for the Zimmermann-Reinhardt method, were analyzed. The true iron content of the ferric oxide samples was determined by reducing a weighed quantity in pure hydrogen and dissolving the iron obtained in dil. sulfuric acid, in an atmosphere of carbon dioxide, then titrating the solution with approximately 0.1 *N* permanganate solution which had been standardized by titration with sodium oxalate. The results are shown in Table IV.

TABLE IV

TITRATION OF FERRIC OXIDE, REDUCED BY STANNOUS CHLORIDE

Wt. of Fe_2O_3, g....	0.2789[a]	0.1969[a]	0.2827[a]	0.3816[a]	0.1895[b]	0.2238[b]	0.2668[b]	0.3000[b]
0.1 *N* $K_2Cr_2O_7$, cc.	34.99	24.73	35.44	47.85	23.52	27.76	33.10	37.19
Fe, %...........	70.05	70.13	70.00	70.02	69.31	69.27	69.28	69.23

[a] Sample A; average of 6 analyses of true Fe content gave 70.01%, max. 70.05%; min. 69.97%.

[b] Sample B; average of 4 analyses of true Fe content gave Fe = 69.30%; max., 69.33%; min., 69.25%. The sample also contained a little $Fe(OH)_3$.

The method was next applied to iron wire, in which the true iron content was determined by difference. The weighed sample was dissolved in hydrochloric acid and potassium chlorate added; the solution was then reduced with stannous chloride and titrated with dichromate solution.

TABLE V

ANALYSIS OF IRON WIRE

Wt. of sample[a].......	0.1162	0.1229	0.1787	0.2549	0.2576
0.1 *N* $K_2Cr_2O_7$, cc.....	20.73	21.99	31.86	45.40	45.87
Fe, %..............	99.62	99.73	99.56	99.46	99.43

[a] Composition of sample: C, 0.09%; S, 0.005%; P, 0.02%; Mn, 0.11%; Si, 0.02%; Cu, 0.06%; As, 0; total, 0.305%; Fe (by difference), 99.695%.

The results show that the end-point with diphenylamine as indicator is very sharp in solutions which have been reduced by stannous chloride.

Finally, some results obtained in the determination of iron in ores may be given, for the purpose of further comparing the Zimmermann-Reinhardt, method with the diphenylamine method. About 1 g. of ore was digested in 20 cc. of concd. hydrochloric acid at 70–80°, the solution diluted with an equal volume of water, and filtered; the insoluble residue, still containing a small quantity of iron, was fused with sodium carbonate in a platinum crucible. The melt was dissolved in dil. hydrochloric acid and the iron precipitated with aqueous ammonia. The ferric hydroxide was filtered off and dissolved in a few cubic centimeters of dil. hydrochloric acid, this solution being then added to the original filtrate. Aliquot portions of the solution were then taken for titration. In Table VI, the results in the columns headed Lab. I and II are those obtained by the usual permanganate method as carried out in the laboratories of works which were kind enough to send me the samples, while the last three columns give the results obtained by the diphenylamine method.

TABLE VI

ANALYSIS OF IRON ORES

Sample	Lab. I Fe %	Lab. II Fe %	Wt. sample (dry) G.	0.1 N $K_2Cr_2O_7$ Cc.	Fe %
Roasted siderite fr. N. Hungary	43.16	43.26	0.1988	15.36	43.15
			.3976	30.71	43.13
Swedish magnetic iron ore fr. Dalarne	63.13	63.46	.2998	33.98	63.27
Swedish magnetic iron ore fr. Grangesberg	60.23	59.85	.2205	23.62	59.81
			.2205	23.64	59.86
Puddling slag from Bohemia	56.41	56.14	.3988	40.15	56.22
			.3988	40.12	56.19

The small quantity of platinum which dissolves in the melt during the fusion of the insoluble residue does not affect the results of titration, unless the quantity exceeds 0.1 mg. of platinum. For exact analyses the platinum must be removed by the addition of hydrogen sulfide before titration. Table VII shows the effect of platinum on the titration of iron reduced by stannous chloride.

TABLE VII

INFLUENCE OF PLATINUM ON TITRATION

20 cc. of approximately 0.1 N $FeCl_3$ solution was taken

Pt, mg	...	0.1	0.2	0.3	0.5	1.0
0.1 N $K_2Cr_2O_7$, cc	20.20	20.27	20.33	20.40	20.59	20.90
Diff., cc	...	+0.07	+0.13	+0.20	+0.39	+0.70

Summary

1. The use of diphenylamine as indicator in the titration of iron with dichromate solution (Penny's method) avoids the defects of the original method and increases the accuracy of the determination of iron.
2. The diphenylamine method is much less dependent on the proportion of iron taken than are other methods.
3. The method permits back-titration.

4. The titration of iron salts which have been reduced by stannous chloride is rapid and very accurate, the method being preferable to the Zimmermann-Reinhardt method.

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THE DECOMPOSITION OF POTASSIUM CHLORATE AND ITS CATALYSIS BY POTASSIUM CHLORIDE

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Introduction

Two well-known reactions take place independently and simultaneously when potassium chlorate is heated: (1) $4KClO_3 = 3KClO_4 + KCl$; (2) $2KClO_3 = 2KCl + 3O_2$. A third reaction, (3) $KClO_4 = KCl + 2O_2$, ensues at higher temperatures. A recent paper of the authors[2] presented the kinetics of Reaction 3 and its catalysis by ferric oxide. The present paper is concerned with the kinetics of Reactions 1 and 2 and the autocatalysis of Reaction 1 by potassium chloride, a product common to both reactions.

A review of the previous investigations,[3] which have purposed to derive mathematical expressions for the experimental results, presents a maze of complications due to the fact that different temperatures and various concentrations of catalysts affect in a widely different manner the speed of the simultaneous and independent reactions 1, 2 and 3.

The repeated statement that chlorine is a by product in the decomposition by heat of potassium chlorate and of potassium perchlorate[4] is refuted by the work of Wagner[5] and the present authors who, using pure compounds, could detect no free chlorine.

A further difference in results was reported by Marignac[6] who, working with open tubes and no temperature regulation, found that the presence of potassium chloride and potassium perchlorate occasioned a decrease

[1] Abstract of the second part of the thesis presented by Carl E. Otto to the Faculty of the Graduate School, University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Otto and Fry, THIS JOURNAL, **45,** 1134 (1923).

[3] Teed, *J. Chem. Soc.*, **51,** 283 (1887); Abstr. of *Proc. Chem. Soc.*, **1,** 141 (1885). Potilitzin, *J. Chem. Soc.*, **54,** 219 (1888). Franklin and Dingwall, *ibid.*, **51,** 274 (1887). Mills, *Phil. Mag.*, **23,** 375 (1887); *J. Chem. Soc.*, **52,** 767 (1887). Sodeau, *ibid.*, **81,** 1067 (1902).

[4] Sodeau, *J. Chem. Soc.*, **77,** 137 (1900). Spring and Prost, *Bull. soc. chim.*, **1,** 340 (1889); *J. Chem. Soc.*, **56,** 1105 (1889). Sodeau, *Chem. News*, **80,** 8 (1899). Fowler and Grant, *J. Chem. Soc.*, **57,** 272 (1890).

[5] Wagner, *Z. anal. Chem.*, **21,** 508 (1882).

[6] Marignac, *Bib. Univ. Geneva*, **45,** 346 (1843).