STANDARDIZATION OF PERMANGANATE SOLUTIONS WITH SODIUM OXALATE

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ABSTRACT

The titer of permanganate solutions standardized with sodium oxalate by the procedure usually employed (McBride's) has been found to be too high when compared with the values obtained with other primary standards, the error in some cases being as much as 0.4 percent. However, by modifying this procedure the titer obtained with oxalate agrees satisfactorily with the values found with potassium dichromate, pure iron, and arsenious oxide. In the recommended procedure, 90 to 95 percent of the permanganate is added rapidly to a diluted sulphuric acid (5+95) solution of sodium oxalate at 25 to 30° C, the solution warmed to 55 to 60° C and titration completed as usual. Data are presented which show the effect on the new procedure of variations in acidity, temperature, and other conditions.

CONTENTS

I. INTRODUCTION

The procedure generally used in the standardization of permanganate solutions $(0.1N)$ with sodium oxalate is that described by R. S. McBride.[1] In this method sodium oxalate is dissolved in 250 ml of diluted sulphuric acid $(2+98)$[2] and titrated at an initial temperature of 80 to 90° C and a final temperature of not less than 60° C. Further, it is specified that (1) the solution must be stirred vigorously and continuously, (2) the permanganate must not be added more rapidly than 10 to 15 ml per minute, and (3) the last 1 ml must be added dropwise, allowing each drop to become completely decolorized before the next is added. McBride did not cite any data as to the accuracy of this procedure based on comparisons with other primary standards, but concluded from other considerations that the error in the recommended method should not exceed 0.1 percent.

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[1] J. Am. Chem. Soc. **34**, 393 (1912).

[2] Throughout this paper diluted acids will be designated as in the following example, "diluted sulphuric acid $(2+98)$" will mean 2 volumes of the concentrated acid of specific gravity 1.84 diluted with 98 volumes of water.

In his study of the effect of temperature, acidity, rate of addition of permanganate, and other variables, McBride found, as has also been the experience of others, that the titer varies according to the method employed. Consequently, the titration procedure necessary for obtaining an accurate titer must be determined empirically by comparison with other suitable standards.

I. M. Kolthoff [3] has also critically examined the permanganate titration. He recommends a procedure [4] much like that of McBride but makes no specific statement in regard to the rate of addition of permanganate, except to say that it must be added slowly in the beginning. He states that titers so obtained agree within 0.05 percent with those found by means of other primary standards.[5] As will be shown later in this paper, the titer is affected by the rate of addition of permanganate, especially when the titration is made in a hot solution. The excellent agreement claimed by Kolthoff may be due in part to rapid titration, since he states [6] that 100 ml of permanganate was added in three to four minutes. We have found that the titer obtained by Kolthoff's procedure when permanganate (approximately 0.1N) is added at a rate of 10 to 15 ml per minute is about the same as that found by McBride's method.

Within the past decade data have accumulated which indicate that the titer of a permanganate solution obtained by McBride's method is from 0.1 to 0.4 percent higher than that found with potassium dichromate through ferrous sulphate.[7] Objections have sometimes been raised in regard to the suitability of potassium dichromate as a primary standard, but recently H. H. Willard and P. Young [8] have shown that the carefully prepared salt is an excellent standard.

Recently, in the analysis of an iron ore (National Bureau of Standards Standard Sample No. 27b), the iron values obtained by titration with a solution of permanganate standardized by McBride's procedure averaged about 0.2 percent higher than those found with solutions prepared from recrystallized and fused potassium dichromate.

This situation led us to make a critical comparison of the titer obtained by McBride's method with that secured by means of other primary standards. As shown in table 1, it was found that the titer given by McBride's method ranged from about 0.2 to 0.45 percent higher than that obtained with potassium dichromate, with pure iron, and with arsenious oxide. In these tests it was observed that small deviations from McBride's directions changed the titer obtained by his method. Such deviations, often made unintentionally, no doubt account for the fact that some analysts apparently have obtained accurate titers by McBride's method.

[3] Z. anal. Chem. **64**, 185 (1924).
[4] I. M. Kolthoff and N. H. Furman, Volumetric Analysis, **2**, 285 (J. Wiley and Sons, 1929).
[5] Z. anal. Chem. **64**, 255 (1924).
[6] Page 196 of reference given in footnote 3.
[7] M. Eppley and W. C. Vosburgh, J. Am. Chem. Soc. **44**, 2148 (1922); H. H. Willard and R. C. Gibson, Ind. Eng. Chem., Anal. Ed. **3**, 88 (1931); Sampling and Analysis of Pig Iron and Cast Iron, Carnegie Steel Co. Bureau of Technical Instruction, p. 103, 3d ed. (1934); R. F. Jackson, Unpublished tests, National Bureau of Standards (1934).
[8] Ind. Eng. Chem., Anal. Ed. **7**, 57 (1935).

TABLE 1.—*Comparison of results obtained by standardizing permanganate solutions according to McBride, and by the use of certain primary standards*

KMnO₄ solution	Oxalate by McBride's procedure			Recrystallized K₂Cr₂O₇ through FeSO₄			Pure iron			Arsenious oxide		
No.	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]
			%			%			%			%
1	0.11066	3	0.03	0.11045	4	0.04	0.11042	2	0.03			
2	.11009	5	.04	.10956	5	.01						
3	.10114	5	.04				.10066	2	.01			
4	.10655	4	.06				.10621	1				
7	.09845	2	.03							0.09811	5	0.02

[1] A. D.=Average deviation from the mean.

The errors in question are outside the limits of accuracy as determined by the end-point corrections and by uncertainties in the atomic weights. While not significant in most commercial work, they are of moment in intercomparisons of primary standards and in certain volumetric analyses such as the determination of iron in materials like high-grade iron ores.

II. DISCUSSION OF THE PERMANGANATE-OXALATE REACTION

The kinetics of the permanganate-oxalate reaction has been studied by a number of investigators, in particular more recently by H. F. Launer and D. M. Yost.[9] It has been shown that the reaction is quite complex and proceeds in several steps, involving compounds containing manganese with valencies intermediate between seven and two, before the end products, carbon dioxide and water are obtained. Atmospheric oxygen also takes part in the reactions.

The concentrations, acidities, etc., employed in these kinetic studies have in general been different from those customarily used by the analytical chemist; consequently he cannot predict from these data but must determine directly the effect of any changed condition on the permanganate-oxalate titer.

McBride determined the effect on the titer of several variations in the titration procedure. His data show that higher titers are obtained both by increasing the temperature and by decreasing the acidity. For example, in diluted sulphuric acid (2+98) the titer was about 0.1 percent higher at 85° C than at 30° C. As regards acidity he found that at 85° C the titer was approximately 0.12 percent higher in (2+98) than in (5+95) diluted sulphuric acid. We have confirmed McBride's findings and have observed further that variations in the acidity cause larger differences in the titer at 85° C than at 30° C.

The titer is also affected by the rate of adding the permanganate, more particularly in hot solutions. McBride found (after the initial reduction of 3 to 10 ml of permanganate) that the titer obtained when the titration was completed in 0.5 minute in diluted sulphuric acid (2+98) at 90° C, was about 0.2 percent less than that found in 5

[9] J. Am. Chem. Soc. 56, 2571 (1934).

minutes under similar conditions.[10]   We have found that the titer obtained in diluted sulphuric acid $(2+98)$ at 85° C when the permanganate is added at a rate of 10 ml per minute is consistently higher (approximately 0.10 to 0.15 percent) than that found when the rate of addition is 20 ml per minute.   At 30° C, McBride found little variation in titer with the rate of titration in solutions containing either 2 or 5 ml of sulphuric acid (sp gr 1.84) per 100 ml.

K. Schröder,[11] who also studied this titration, recommended that "The greater part of the permanganate be rapidly run into a strongly acidified solution of the oxalate at 50° C and the titration finished more slowly."   McBride, however, concluded that the conditions recommended by Schröder led to a "loss of oxygen."

The rate of stirring also influences the titer.   We have observed that rapid motor-stirring yields different values in hot solutions than does stirring by hand.   The apparent titer rises with an increase in the agitation of the solution.   This effect is especially noticeable when the permanganate is added slowly.   At a rate of 10 ml per minute we have observed differences of 0.10 percent or more caused by variations in the rate of stirring.[12]

Several investigators have shown that peroxides are formed during the oxidation of oxalic acid by permanganate.   Schröder showed that diluted sulphuric acid solutions of oxalate containing manganous-ion react with air to form peroxide.   Launer [13] has shown that oxygen is absorbed, peroxides are formed, and carbon dioxide in excess of the theoretical amount is evolved when an excess of oxalic acid reacts at 25° C with manganous, manganic, and fluoride ions in an acid solution in the presence of air.   He observed that for each mole of oxygen absorbed two moles of carbon dioxide were produced, a reaction for which he suggests the following equation:

$$O_2 + C_2O_4^= + 2H^+ = H_2O_2 + 2CO_2$$
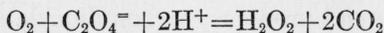
Kolthoff [14] has shown that the amount of peroxide formed when oxalate is partially titrated with permanganate increases with rise in temperature and with manganous-ion concentration.   He found that no peroxide is formed when titrations are made in an atmosphere of nitrogen with all solutions freed from oxygen.   Since peroxide reacts with permanganate before a permanent pink end point can be obtained, an amount of permanganate equivalent to the oxalic acid oxidized by air should be consumed, provided none of the peroxide escapes.

Not all the error in the titer can be accounted for by peroxide formation; if the reaction is performed in an atmosphere of nitrogen, with solutions carefully freed from oxygen, there is still a difference found between rapid titration at 30° C and slow titration at 85° C. For example, our data indicate that even in nitrogen rapid titration

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[10] We have found that when titration was made in diluted sulphuric acid (2+98) at 85° C at the maximum rate (i. e., by adding rapidly 99.8 percent of the permanganate from a small beaker and then completing the titration), the titer so obtained averaged about 0.2 percent lower than the value secured by titrating at 10 to 15 ml per minute.

[11] Z. öffentl. Chem. **16**, 270 (1910).

[12] There also appears to be a difference in the titer obtained by McBride's method (i. e., slow titration in hot dilute sulphuric acid (2+98)) in erlenmeyer flasks as compared with beakers.   We have found that titers so obtained in a 500-ml erlenmeyer flask may range from 0.05 to 0.15 percent lower than those secured in a 400-ml beaker.

[13] J. Am. Chem. Soc. **55**, 865 (1933).

[14] Z. anal. Chem. **64**, 185 (1924).

in diluted sulphuric acid (5+95) at 30° C (our recommended procedure) yielded titers about 0.2 percent lower than those obtained by slow titration in diluted sulphuric acid (2+98) at 85° C (McBride's procedure).

To sum up, titers tend to be high if titration is made at high temperature, in low acidity, and with slow addition of permanganate accompanied by rapid stirring. In this connection it is perhaps well to point out that McBride has shown that (1) no oxalic acid remains at the end of the reaction, (2) the residual oxidant is no more than the amount required to give the end-point color, and (3) no volatilization of oxalic acid occurs during titration at temperatures below 90° C. Further, Kolthoff [15] found that (4) no significant amounts of oxygen or carbon monoxide could be detected when oxalate was titrated slowly in hot dilute sulphuric acid. It would appear therefore that the above-mentioned factors are eliminated as causing high titers.

III. RECOMMENDED PROCEDURE

Consideration of the foregoing data (section II) indicated that rapid titration at lower temperatures should yield lower titers. Experiments were therefore initiated to examine the magnitude of error when the reaction is conducted at room temperature. At 30° C the reaction in diluted sulphuric acid (2+98) is rather slow. However, when most of the permanganate is added rapidly in diluted sulphuric acid (5+95) at 25 to 30° C and the titration then completed at 55 to 60° C, no end-point difficulties are encountered. A procedure based on these conditions was developed and, as shown later (section IV–2), was found to yield titers that agree well with those obtained with other primary standards.

Procedure.—Transfer 0.3 g of sodium oxalate (dried at 105° C) to a 600-ml beaker. Add 250 ml of diluted sulphuric acid (5+95) previously boiled for 10 to 15 minutes and then cooled to $27 \pm 3°C$. Stir until the oxalate has dissolved. Add 39 to 40 ml [16] of $0.1N$ potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds).[17] Heat to 55 to 60° C, and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise with particular care to allow each drop to become decolorized before the next is introduced.

Determine the excess of permanganate required to impart a pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the boiled and cooled diluted sulphuric acid at 55 to 60° C. This correction usually amounts to 0.03 to 0.05 ml.[18]

In potentiometric titrations the correction is negligible if the end point is approached slowly.

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[15] Z. anal. Chem. **64**, 185 (1924).

[16] 0.3 g of sodium oxalate requires 44.73 ml of $0.1N$ KMnO$_4$.

[17] If the pink color should persist because the permanganate is too strong, discard, and begin again, adding a few milliliters less of the KMnO$_4$ solution.

[18] In very accurate work the correction is best obtained iodometrically (W. C. Bray, J. Am. Chem. Soc. **32**, 1204 (1910)) as follows: cool the titrated solution to 25° C, add 0.5 g of KI, 2 ml of starch solution, and titrate the liberated iodine with $0.02N$ thiosulphate. To obtain the ratio of the thiosulphate to the permanganate solution, add 1 ml of the $0.1N$ permanganate to 300 ml of the diluted sulphuric acid (5+95), stir, add 0.5 g of KI, and titrate with thiosulphate solution, adding starch just before the end point is reached.

IV. TESTS OF THE RECOMMENDED PROCEDURE

1. REAGENTS AND SOLUTIONS

Potassium Permanganate.—Potassium permanganate of reagent quality from several commercial sources was used to prepare solutions that were approximately $0.1N$ and contained 0.1 percent of potassium hydroxide. After aging for at least two weeks the solutions were filtered through purified asbestos into a bottle protected from light. As portions were required for use they were withdrawn through a siphon. The air used to displace the permanganate was passed through glass cotton and alkaline permanganate to remove dust and acid fumes.

Sodium Oxalate.—The sodium oxalate used in this investigation was the National Bureau of Standards Standard Sample No. 40c. Its reducing power was calculated from the certificate analysis as 99.95 percent of the theoretical. Samples were always thoroughly dried at 105 to 110° C immediately before use.

Potassium Dichromate.—Potassium dichromate of reagent quality from two commercial sources was recrystallized twice in platinum. The crystals were dried at 105° C and finally fused in a covered container at 400° C in an electric muffle. The granular salt was preserved in a desiccator, and dried for a short time at 105 to 110° C immediately before use. Approximately $0.1N$ solutions were prepared from accurately weighed amounts of the salt and distilled water.

Pure Iron.—Through the courtesy of the Metallurgy Division of this Bureau, we were fortunate in securing for this work iron wire of very high purity prepared by H. E. Cleaves in connection with another project. While no complete chemical analysis has been made of this material, spectrochemical examination showed faint traces of calcium, magnesium, aluminum, and silicon as the only impurities. The gas content was found to be less than 0.005 percent. The purity of this wire is believed to be at least 99.98 percent. The wire was carefully polished with the finest emery cloth to remove any trace of surface oxide and thoroughly wiped with filter paper immediately before use.

Arsenious Oxide.—The arsenious oxide was the National Bureau of Standards Standard Sample No. 83. Its reducing power was taken as 99.98 percent from the certificate issued with this standard.

Ferrous Ammonium Sulphate.—Solutions approximately $0.1N$ in ferrous iron and containing 10 ml of sulphuric acid per liter were made from ferrous ammonium sulphate of reagent quality. They were saturated with and stored under nitrogen or carbon dioxide.

0.01M Osmium Tetroxide.—0.5 g of osmium tetroxide was dissolved in 200 ml of diluted sulphuric acid (3+97).

Blank determinations were made on the distilled water and acids used. Weight burettes were used in all titrations, so the normalities given in the tables are in gram equivalents per gram of solution. All weights were reduced to vacuum for the intercomparisons. Intercomparisons of the permanganate with other standards were always made within the same day to avoid errors caused by any loss of its oxidizing power.

2. COMPARISON OF THE OXALATE TITER WITH THOSE OBTAINED WITH OTHER PRIMARY STANDARDS

The best proof of the accuracy of titers of volumetric solutions is obviously the agreement obtained by means of different primary standards through reactions that are simple, known to be quantitative, and not affected by slight changes in the procedure used for the standardization. The oxidation of ferrous iron with either permanganate or dichromate is a reaction of this character. Therefore, if the titers of permanganate solutions based on sodium oxalate agree with those found with pure iron and with potassium dichromate, then the oxalate titer by the procedure used is very probably accurate within the errors of the comparison.

The standardization of the permanganate by means of the dichromate was made by titrating 50- to 60-g portions of approximately $0.1N$ ferrous ammonium sulphate in a volume of 300 ml of diluted sulphuric acid $(5+95)$ with each of the two oxidizing agents; the theoretical titer of the dichromate was calculated from its weight.

The end points were determined potentiometrically.

The following procedure was used in obtaining the titer of the permanganate solution by means of pure iron:

0.3- to 0.35-g portions of the iron were dissolved in approximately 100 ml of diluted sulphuric acid $(20+80)$ which had been boiled and cooled under carbon dioxide. To prevent loss by spraying, the wire was dissolved in a flask fitted with a vertical condensing arrangement to wash all escaping gas. A slow stream of carbon dioxide was passed through the flask during the whole operation. After the wire had dissolved, the solution was cooled to $25°$ C and about 90 percent of the iron was titrated in the flask in an atmosphere of carbon dioxide. The solution was then transferred to a beaker and the titration finished potentiometrically under carbon dioxide. The final volume was 300 to 400 ml and contained from 5 to 10 ml of sulphuric acid (sp gr 1.84) per 100 ml of solution. The end point was approached by adding 0.01- to 0.02-ml increments of solution, and the maximum change in potential was taken as the end point.

The dichromate and pure iron were also compared by the method described in the preceding paragraph. It will be noted in table 2 that the agreement between these two standards is within the usual experimental error.[19]

TABLE 2.—*Titration of iron with* $K_2Cr_2O_7$

Wt Fe taken	Fe found	Difference	Error	Remarks
g	g	mg	%	
0.3000	0.2999	−0.1	−0.03	Titrated with $K_2Cr_2O_7$ solution prepared from lot 1.
.3509	.3508	−.1	−.03	Do.
.3504	.3505	+.1	+.03	Do.
.3520	.3518	−.2	−.06	Do.
.3322	.3322			Titrated with $K_2Cr_2O_7$ solution prepared from lot 2.
.3342	.3342			Do.

[19] It has been reported that the end point obtained when ferrous iron is titrated potentiometrically with dichromate varies with the concentration of iron and with the acidity. This is true in part, but the effect is significant only when titrations are made in relatively small or large volumes. Our data show that titrations made in a volume of 350 to 400 ml of diluted sulphuric acid $(5+95)$ to $(10+90)$ are independent of amounts of iron between 0.1 and 0.5 g.

The titer through arsenious oxide was obtained by K. Gleu's method,[20] in which osmium tetroxide is employed as a catalyst. The following procedure was used: 0.3 g of arsenious oxide was transferred to a 600-ml beaker and 10 ml of a sodium hydroxide solution (20 g of NaOH to 100 ml of water) was added. When the arsenious oxide had completely dissolved, 200 ml of diluted sulphuric acid (3+97), previously boiled and cooled, and 5 drops of 0.01M osmium tetroxide were added. The solution was then titrated with permanganate. The last 5 to 6 ml were added dropwise [21] and the end point determined potentiometrically.

Table 3 shows that the maximum difference between the titer of permanganate solutions based on sodium oxalate and the recommended procedure, and those found with potassium dichromate, pure iron, and arsenious oxide is 0.06 percent. It appears therefore that the recommended procedure leads to a consumption of permanganate very closely in accordance with the equation,
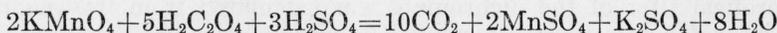
$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

TABLE 3.—*Comparison of results obtained by standardizing permanganate solutions according to the recommended procedure, and by the use of certain primary standards*

KMnO₄ solution no.	Oxalate by recommended procedure			Recrystallized K₂Cr₂O₇ through FeSO₄			Pure iron			Arsenious oxide		
	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]	Normality	No. of determinations	A. D.[1]
			%			%			%			%
5	0.11850	5	0.01				0.11843	2	0.02			
6	.12471	2	.01	0.12472	3	0.03						
7	.09816	7	.02	.09816	4	.02				0.09811	5	0.02
8	.09810	6	.01				.09810	4	.05			
9	.10322	4	.02							.10319	9	.02

[1] A. D.=average deviation from the mean.

3. EFFECT ON THE RECOMMENDED METHOD OF VARIATIONS IN THE DESCRIBED PROCEDURE

Titers obtained by McBride's method have been shown to vary significantly as the rate of adding permanganate, the acidity, and other conditions are changed. Table 4 presents data showing the effects of these variables in the recommended procedure.

[20] Z. anal. Chem. **95**, 305 (1933).

[21] Our tests indicated that an excess of permanganate is consumed if the latter part of the titration is made too rapidly.

TABLE 4.—*Effect of small departures from the recommended procedure*

[Titer obtained by recommended procedure =0.12471*N*]

Temperature (°C)	Normality
15	0. 12466
19	. 12470
31	. 12472
36	. 12482
Rate: KMnO₄ per minute (ml)	
20	. 12472
10	. 12482
Total KMnO₄ added at start (%)	
50	. 12480

It will be noted that the temperature effect is negligible between 20 and 30° C. Above 30°, the titer begins to increase slowly. Further, the rate of addition of the first portion of the permanganate has little effect on the titer, provided 90 to 95 percent of the permanganate required is added at a rate above 20 ml per minute. Decreasing the rate of addition of the initial portion to 10 ml per minute yields a small increase in the titer. An initial addition of only 50 percent of the required permanganate raises the titer slightly, so, as previously mentioned, it is desirable to add 90 to 95 percent of the permanganate at the start of the titration.

The titer is only slightly affected by a moderate increase in acidity above that recommended. For example, titrations in diluted sulphuric acid (10+90) indicated a titer about 0.05 percent lower than that obtained by the recommended procedure.

Any large increase in the manganous-ion concentration tends to raise the apparent titer although small amounts cause only a slight change. An addition of manganese sulphate, equivalent to 10 ml of a 0.1*N* permanganate, added at the start of a titration, caused no significant change in the titer, though it reduced the time required for the initial clearing of the solution by 50 percent.

V. SUMMARY

McBride's method for the standardization of permanganate solutions with sodium oxalate (i. e., slow titration in hot diluted sulphuric acid (2+98)) yields titers that are too high, the error in some cases being as much as 0.4 percent.

A procedure is recommended for the exact standardization of permanganate with sodium oxalate. In this method 90 to 95 percent of the permanganate is added rapidly to a diluted sulphuric acid (5+95) solution of the oxalate at 25 to 30° C, the solution warmed to 55 to 60° C and the titration completed, the last 0.5 to 1 ml portion being added dropwise. The titer so obtained agrees with those found by means of other primary standards within the limits of experimental error.

WASHINGTON, September 20, 1935.