TABLE III.—ANALYSIS OF BADDELEYITE.

Weight of sample, g.	SiO_2 found, %.	Fe_2O_3 found, %.	ZrO_2 found, % PO_4 method.	TiO_2 found, % calorimetrically.	Al_2O_3 found, %.	MnO_2 found, %.	H_2O found, % (average).	Total found, %.
0.5016	15.83	2.31	71.46	0.78	5.24	0.98	2.94	99.54
0.5017	15.73	2.55	71.15	0.76	5.56	0.92	2.94	99.61
0.5006	15.46	2.66	71.23	0.75	5.82	1.12	2.94	99.98
0.5006	15.72	2.44	71.35	0.75	5.46	0.75	2.94	99.41

Summary.

The above results show that the cupferron reagent may be used in acid solution for the quantitative precipitation of iron, titanium, and zirconium from solutions containing these elements mixed with aluminum and manganese. The first three of these elements may be separated by standard methods, as by the procedures outlined above. The aluminum and manganese may be determined by standard methods after the removal of the excess cupferron.

Analyses were made both of mixed solutions of pure salts and of minerals, with accurate results.

Recognition is due R. B. Moore, of the United States Bureau of Mines, for suggesting the analysis of zirconium minerals as an inviting field for investigation.

INDIANAPOLIS, IND.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE COLORIMETRIC DETERMINATION OF MANGANESE BY OXIDATION WITH PERIODATE.[1]

BY HOBART H. WILLARD AND LUCIEN H. GREATHOUSE.

Received July 23, 1917.

Historical.

The determination of manganese by comparing the color intensities of solutions of the permanganate ion has been a practical method for the rapid estimation of small amounts for about forty-five years. W. Crum[2] first suggested the possibility of using in this way the oxidation of manganous salts to permanganate by means of lead dioxide in nitric acid solution, but P. Pichard[3] was the first to work out the details for a complete method. A number of communications appearing in the thirty years following Pichard's work, proposed or discussed methods which utilized the same principles. Reactions involving other colored compounds of manganese have been proposed (references 4, 8, 13, 14, 15 in the bibliography) but have never found much favor.

---

[1] Read at the meeting of the American Chemical Society in Cincinnati, April, 1914.

[2] *Ann.*, **55**, 219 (1845).

[3] *Compt. rend.*, **75**, 1821 (1872).

Hugh Marshall[1] presented the first variation that was destined to be widely used. He replaced lead dioxide by an alkali persulfate, using silver ion as a catalyzer. This change eliminated from the procedure the filtration to remove the excess of reagent. It had the further advantage that the persulfate could easily be prepared free from manganese.

The persulfate method has long been recognized as being erratic; the true permanganate color is not always obtained and oxidation is often incomplete.[2] The color frequently fades after a short time. Fairly close control of the time of heating and of the concentration of acid and of manganese is necessary to obtain accurate results and to prevent the formation of manganese dioxide. Traces of chloride give an opalescence of silver chloride which must be coagulated and filtered off before comparison can be made. In spite of these disadvantages the method is widely used and the Chemists' Committee of the U. S. Steel Corporation[3] included it among the standard methods for iron and steel analysis.

Another oxidizing agent which has been much used and which is more reliable in its action than persulfate is sodium bismuthate. Its use for this purpose was first proposed by Reddrop and Ramage[4] in 1895, six years before the persulfate reaction was known, but it seems to have been unnoticed or forgotten until Dufty[5] in 1901 again called attention to it. The excess of this reagent must, however, be separated before comparison.

A complete bibliography of the literature on the colorimetric determination of manganese is given at the end of this article.

The New Method.

The method described in the following pages is free from all the faults of previous methods and is based upon an entirely new reaction—the oxidation in acid solution of manganous salts to permanganate by means of periodic acid or its salts; the latter are reduced to the form of iodate. The reaction is represented by the following equation:

$$2Mn(NO_3)_2 + 5KIO_4 + 3H_2O = 2HMnO_4 + 5KIO_3 + 4HNO_3$$

Only a small excess of periodate is required, but the success of the reaction depends upon the presence of a sufficient concentration of acid, otherwise precipitation occurs, and the product varies widely according to conditions. This accounts for the conflicting results reported by previous investigators. The minimum concentration of acid required increases with the concentration of manganese.

---

[1] *Chem. News,* 83, 76 (1901).

[2] Gortner and Rost, *J. Ind. Eng. Chem.,* 4, 522; Applebaum, *Chem. Analyst,* No. 17, 22.

[3] *J. Ind. Eng. Chem.,* 4, 807 (1912).

[4] *J. Chem. Soc.,* 67, 275 (1895), footnote.

[5] *Chem. News,* 84, 248 (1901).

Langlois[1] stated that periodic acid was reduced to iodic acid by manganous salts and that a precipitate of manganic iodate was formed.

Rammelsberg[2] found that a precipitate of hydrated manganese dioxide formed in neutral solution.

W. B. Price[3] isolated and analyzed several brick-red precipitates formed in dilute nitric or sulfuric acid solution. From his results he calculated formulas for complex sodium, potassium and possibly hydrogen, manganic (trivalent) periodates.

S. R. Benedict[4] suggested the use of potassium periodate in neutral or ammoniacal solution as a reagent for the detection of manganese. The compounds already described by Price[5] served to indicate manganese when present in considerable amounts, while in very dilute solutions of manganese a red coloration appeared, which Benedict designated as "the characteristic color of manganese periodate," although he mentioned no experiments in support of this view.

In studying the reactions between periodate and salts of manganese the qualitative effects described earlier were, in general, found to be correct. However, the coloration produced in solutions of low manganese content, ascribed by Benedict to a compound containing iodine, proved to be due only to the permanganate ion, and this reaction always occurs if sufficient acid is present, even with considerable amounts of manganese.

The reliability of this reaction led to the idea that periodate might, with advantage, be substituted for persulfate in the colorimetric determination of manganese. To test the method the effects of temperature and of varying concentrations of sulfuric, nitric and phosphoric acids, of ammonium salts, chlorides, manganese and periodate were observed by comparing standard solutions containing only chemically pure substances free from heavy metals. These experiments demonstrated the reliability of the method. It was then applied to steels and iron ores, since standardized samples of these materials were available. The results in all cases were entirely satisfactory. Attempts to utilize this reaction in a volumetric method for manganese, similar to the persulfate-arsenite titration, were unsuccessful, since the excess of the reagent cannot be removed, and any reducing agent that may be used to titrate the permanganate instantly reduces the periodate as well.

Experimental.

A standard solution of manganese sulfate containing 0.1 mg. of manganese per cc. was made by reducing an accurately measured volume of

---

[1] *Ann. chim. phys.*, [3] **34**, 257 (1852).

[2] *Ann. Phys. Chem.*, **134**, 528 (1868).

[3] *Am. Chem. J.*, **30**, 182 (1903).

[4] *Ibid.*, **34**, 581 (1905).

[5] *Loc. cit.*

standard permanganate with sulfur dioxide, expelling the excess by boiling, and, after cooling, diluting to the proper volume. The permanganate solution had been prepared by dissolving the "analyzed" salt of a well-known manufacturer in water which had been distilled from alkaline permanganate and redistilled. This solution, which was very stable, had been standardized against samples of sodium oxalate and iron ore of known iron content obtained from the Bureau of Standards, both methods showing excellent agreement.

The acids used—sulfuric, nitric, hydrochloric and phosphoric—were chemically pure products; ammonium sulfate and persulfate were the purest grade furnished by a well-known firm. All reagents were carefully tested for manganese and found to be free from it.

The periodate used was the potassium salt, KIO_4, furnished by a European manufacturer. This material showed by analysis the theoretical content of I_2O_7 and qualitative tests indicated no impurities except a trace of sodium. The potassium salt is the only form in which this oxidizing agent is ordinarily sold by dealers. Sodium metaperiodate, $NaIO_4$, would, however, be more serviceable as a reagent on account of its greater solubility. Moreover, the latter can be produced more cheaply under existing conditions and possibly at all times.

The Campbell-Hurley colorimeter[1] was used throughout this work.

The first comparisons made were between a solution containing pure potassium permanganate and those containing the same amount of manganese as sulfate, oxidized in one case by persulfate and in the other by periodate. The two latter solutions were also compared with each other. They were prepared as follows:

Pure permanganate: 4.36 cc. of 0.10428 *N* solution (containing 5 mg. of manganese) diluted to 250 cc.

Persulfate oxidation: 50 cc. manganese sulfate solution (containing 5 mg. of manganese), 15 cc. sulfuric acid (sp. gr. 1.84), 0.2 g. silver nitrate and 2 g. ammonium persulfate, heated to boiling, cooled at once and diluted to 250 cc.

Periodate oxidation: 50 cc. manganous sulfate solution, 10 cc. sulfuric acid, and 0.5 g. potassium periodate, boiled ten minutes, cooled and diluted to 250 cc.

The following colorimeter readings were obtained, the figures representing the relative depths of columns of liquid having the same intensity of color:

TABLE I.

Pure $KMnO_4$.	Persulfate oxidation.	Periodate oxidation.
90	88.5	...
90	...	90
...	88	90

---

[1] Campbell and Hurley, THIS JOURNAL, 33, 1112 (1911).

The solution oxidized by periodate had exactly the same color as pure permanganate, but the one oxidized by persulfate differed slightly in tint.[1] Whether, however, the variation of 1.5 to 2 scale divisions in the readings of the solution oxidized by persulfate is larger than the experimental error is open to question. Evidently the periodate oxidized the manganese completely under these conditions.

Effect of Varying the Concentration of Acid.—The concentration of sulfuric acid was varied as indicated in Table II. The solution during oxidation had a volume of 50 cc. and contained 2.5 mg. of manganese as sulfate. Each solution, after adding periodate, was boiled one minute, then heated on the sand bath for fifteen minutes, after which it was cooled and diluted to 250 cc. The time required for the appearance of the full depth of color was noted. The solution containing 30 cc. of sulfuric acid per 100 cc. was taken as the standard and compared with each of the others.

Table II.

Concentration of H_2SO_4 varied.

2.5 mg. Mn. Volume during oxidation, 50 cc.; 0.25 g. KIO_4 added.

Cc. conc. H_2SO_4 per 100 cc. solution during oxidation.	5	10	15	20	25	30
Time to bring to full color, minutes	12	10	8	6	4	3
Colorimeter reading	91	89	89	90	89	90

A similar set, allowed to stand $1^1/_2$ hours at room temperature, gave partial oxidation, but this reaction did not proceed further in 4 hours, a brick-red precipitate being thrown down instead.

Table III.

Concentration of HNO_3 varied.

5 mg. Mn. Volume during oxidation, 100 cc.; final volume, 250 cc.; 0.3 g. KIO_4 added. Time of heating, 20 min. Standard contained 10 cc. H_2SO_4 but no HNO_3; oxidized in the same way.

Cc. HNO_3 (sp. gr. 1.42) per 100 cc. solution during oxidation	Standard	5.6	16.8	33.7	50
Time to bring to full color, minutes	2	Precipitate formed	6	6	3
Colorimeter reading	90	...	89	90	90

Table IV.

Concentration of H_3PO_4 varied.

Conditions same as in Table III. Same standard.

In each case the full color was developed within 2 or 3 minutes.

Cc. H_3PO_4 (sp. gr. 1.70) per 100 cc. solution during oxidation	Standard	1	5	10	15	30	50
Colorimeter reading	90	90:	90:	90:	90:	90:	90:

In all cases the only effect of increasing the concentration of acid above the minimum required to prevent precipitation is to increase the rate of oxidation of the manganese. This minimum concentration of acid in-

---

[1] See Gortner and Rost, *Loc. cit.*

creases with the concentration of manganese, and varies with different acids, being lowest for phosphoric acid. The well-known stability of manganic phosphates probably accounts for the non-appearance of precipitates of iodates or periodates of manganese even in solutions of very low acid concentration.

Effect of Varying the Concentration of Periodate.—In the following table the theoretical requirement is 0.052 g. Complete oxidation was obtained in every case, even with only 0.1 g. KIO_4, the lower readings corresponding to a greater depth of color. The variation represents the experimental error. The only effect observed was a slight increase in the speed of the reaction as the concentration of periodate was increased.

TABLE V.

5 mg. Mn, 10 cc. conc. H_2SO_4, volume during oxidation 100 cc. Heated 20 min. Full color developed in 3 or 4 min.

KIO_4 added, grams................	Standard	0.3	0.1	0.2	0.4	0.5	0.6
Colorimeter reading...............		90	88	88	89	90	90

Oxidation of Large Amounts of Manganese.—Calculated volumes of tenth normal permanganate were reduced with sulfur dioxide, boiled to remove the excess and diluted to 100 cc. for oxidation. Afterwards they were diluted to the final volumes noted for comparison. The standard was prepared as before, containing 20 mg. of manganese per liter.

TABLE VI.

10 cc. H_3PO_4 (sp. gr. 1.70) in 100 cc. of solution during oxidation.

Mn. Mg.	KIO_4. G.	Time to full color. Min.	Diluted to final volume. Cc.	Reading.	
				Solution.	Standard.
20	1	1–2	1000	90	90
60	2	apparently instantaneous	2000	50	74.5

The complete oxidation of 0.06 g. of manganese in 100 cc. of solution, such as occurred above, cannot be accomplished by any of the other methods. Even larger amounts of manganese can be oxidized, but such solutions are so deeply colored as to be of no practical value.

Effect of Chloride.—Since periodic acid readily oxidizes hydrochloric acid to chlorine according to the equation

$$2HCl + HIO_4 = Cl_2 + HIO_3 + H_2O$$

the complete removal of small amounts of chloride ought to be possible if a sufficient excess of the reagent is added. That this is true is evident from the results given in Table VII.

The last three solutions were heated until the odor of chlorine disappeared.

The ease with which small amounts of chloride can be removed is one of the great advantages of this method.

TABLE VII.

5 mg. Mn, 10 cc. conc. H_2SO_4 in 100 cc. of solution during oxidation. Diluted to 250 cc. for comparison.

0.2 *N* HCl added. Cc.	KIO_4. G.	Time to full color. Min.	Time of heating.	Readings. Solution.	Standard.
0	0.3	2	15 min.	Standard	..
0.2	0.3	2	15 min.	88	90
0.5	0.3	2	15 min.	89	90
5	0.3	3	15 min.	87	90
17	0.5	precipitate	$1^1/_2$ hrs.	..	..
17	0.7	3	$1^1/_2$ hrs.	88	90
50	2.0	3	2 hrs.	89.5	90

Effect of Ammonium Salts.—Although it hardly seemed possible that ammonium salts could interfere, the following experiments were made to test this point: Solutions containing 5 mg. of manganese, 10 cc. of concentrated sulfuric acid, 0.3 g. of periodate, and amounts of ammonium sulfate varying from 5 to 35 g. in a volume of 100 cc. were heated for 20 minutes, cooled, diluted and compared with a standard containing no ammonium salt. In each case the readings showed a ratio of 90 : 89. The presence of the ammonium salt did not affect the intensity of the color, the tint of the solution or the speed of oxidation.

A remarkable feature of the solutions oxidized by periodate is their great stability when a slight excess of the reagent is present. Such a solution, kept for three months in a stoppered flask, when compared with a similar solution freshly oxidized showed no change whatever. This makes it possible to leave the standard solution in the colorimeter, renewing it only occasionally instead of preparing a fresh solution each time, as is necessary when persulfate is used.

The common metals do not interfere in this method except insofar as they themselves impart a color to the solution. The color due to ferric salts may be removed by the addition of phosphoric acid, but to correct for the color due to other metals the same amount must be added to the standard.. A number of metals, such as silver, lead, bismuth and mercury, form iodates or periodates which are insoluble in dilute acids, but by using a high concentration of acid these remain in solution, since the amount of periodate added is small.

If a strong reducing agent such as a ferrous salt is present the periodate will be reduced to free iodine which will color the solution and render it useless. All substances of this kind are removed by boiling or evaporating with nitric acid.

The proper conditions having thus been determined, the method was then further tested by applying it to one of the most common analytical problems—the determination of manganese in iron ore and steel. In many cases the color due to the ferric salt was not removed, but the proper correction was made by adding to the standard the same amount of iron in the form of ferric nitrate. This solution was prepared by dissolving 20 g. of electrolytic iron in nitric acid, evaporating nearly to dryness and diluting to one liter. It contained 1 g. of iron in 50 cc. and by colorimetric determination less than 0.02 mg. of manganese in the same volume. In comparing solutions of the various materials examined, after dilution to suitable volumes, the following standards were used:

TABLE VIII.

Mn added as $MnSO_4$. Fe as $Fe(NO_3)_3$.

Standard.	KIO_4 added. G.	Mn. Mg.	Fe. G.	Conc. H_2SO_4. Cc.	Conc. HNO_3. Cc.	Conc. H_3PO_4. Cc.	Final volume. Cc.
a	0.6	10	1	20	20	..	500
b	0.6	10	2	20	20	..	500
c	0.6	10	0.5	20	20	..	500
d	0.6	10	0	..	..	20	500
e	0.3	5	0	..	..	20	500
f	0.3	5	0	..	..	40	1000

In the series of determinations given in Table IX, samples of iron and steel from the U. S. Bureau of Standards were dissolved in dilute nitric acid containing, for 0.5 g. of metal, 15 cc. of concentrated acid; and for 1 g., 18 cc. Ten cc. concentrated sulfuric acid and the amounts of KIO_4 indicated were then added and the solution, having a volume of about 100 cc., was boiled for a few minutes, cooled, diluted to 250 cc. and compared with the standard containing the same amount of iron.

TABLE IX.

No phosphoric acid added; same amount of iron in standard.

Metal No.	Description of material.	Wt. of sample. G.	KIO_4 added. G.	C present. %.	Mn present. %.	Mn found. %.
1	Basic Open Hearth 1% C. Sample 16	1.0000	0.5	1.05	0.405	0.403
2	Acid Open Hearth 0.1 C. Sample 18	1.0000	0.3	0.10	0.412	0.409
3	Bessemer 0.8 C. Sample 23	0.5000	0.5	0.81	0.775	0.771
4	Acid Open Hearth 0.2 C. Sample 19	0.5000	0.3	0.21	0.760	0.752
5	Bessemer 0.2 C. Sample 9*a*	0.5000	0.3	0.25	0.918	0.913
6	Bessemer 0.4 C. Sample 10*a*	0.5000	0.3	0.45	0.916	0.902
7	Iron D. Sample 6	0.5000	0.3	2.89	1.41	1.407
8	Amer. Foundrymens' Association Iron B	1.0000	0.5	3.11	0.415	0.404

In the series of determinations given in Table X, the same steels were used as in Table IX and are referred to by number only. They were dissolved in nitric acid as before, then 5 or 10 cc. of phosphoric acid (sp. gr. 1.70) and the periodate were added and the solution oxidized as before. The addition of phosphoric acid forms a colorless complex ferric iron, and the resultant solutions diluted to 250 cc. were compared with standard "*d*" to which no iron had been added.

TABLE X.

Phosphoric acid added; no iron in standard.

Metal No.	Weight of sample. G.	KIO_4 added. G.	Mn present. %.	Mn found. %.
1	1.0000	0.5	0.405	0.402
2	1.0000	0.3	0.412	0.412
3	0.5000	0.5	0.775	0.770
4	0.5000	0.3	0.760	0.755
5	0.5000	0.3	0.918	0.905
6	0.5000	0.3	0.916	0.905

These solutions differed only slightly in tint from the pure permanganate standard used, and such comparisons are readily made after a little practice. When more than 1 g. of iron is present its color becomes appreciable, but if the *standard* contains *no* phosphoric acid, the addition to it of 5% of the weight of the iron in the sample gives sufficient color to correct for this.

Occasionally difficulty was caused by variation in tint both with sulfuric and phosphoric acid solutions, arising from the brownish color of the carbon compounds after solution in nitric acid. This effect was especially noticeable where the carbon content was 0.8% or more. Since even a large excess of periodate oxidizes these compounds with difficulty, some means were sought for destroying them before the periodate was added.

Three satisfactory methods were found: (*a*) The sample was dissolved in phosphoric acid and then heated in concentrated solution with 10 cc. of nitric acid. (*b*) It was dissolved directly in a mixture of 10 cc. nitric acid, 10 cc. phosphoric acid, 10 cc. water and boiled until decolorized, most of the water being expelled during this treatment. A little care was necessary at this point to prevent dehydration to a gummy mass that dissolved rather slowly. The concentrated phosphoric acid solution was usually faintly pink, probably due to manganic phosphate. (*c*) The sample was dissolved in a mixture of 15 cc. nitric acid, 15 cc. water and 15 cc. phosphoric acid, 1 g. of ammonium persulfate was added and the solution decolorized by boiling 3 to 5 minutes. Obviously, sulfuric acid can be used instead of phosphoric. This method seems to be the most rapid, the entire determination requiring about 25 minutes. The results with high carbon steels are given in Table XI.

TABLE XI.

Metal No.	Method of decolorizing.	Standard used.	Weight of sample. G.	KIO_4 added. G.	C present. %.	Mn present. %.	Mn found. %.
1	*a*	*d*	1.0000	0.3	1.05	0.405	0.402
3	*a*	*d*	0.5000	0.3	0.81	0.775	0.771
10 High P Steel	*b*	*e*	1.0000	0.3	0.96	0.275	0.278
11 High P Steel	*b*	*e*	1.0000	0.3	1.03	0.286	0.287
1	*c*	*d*	1.0000	0.3	1.05	0.405	0.410

Finally two determinations were made using iron ores of known manganese content. 1 g. samples were dissolved in platinum dishes with 15 cc. phosphoric acid, 5 cc. hydrofluoric acid and a little nitric acid and heated until all fluoride had been volatilized. The resultant mass was dissolved in water, oxidized with 0.3 g. KIO_4 and diluted to 250 cc. The usual method of dissolving the ore in hydrochloric acid could have been used equally well. To expel all choride and to oxidize ferrous salts it is necessary to add 10 cc. of nitric acid and 15 cc. of sulfuric acid and evaporate the solution to fumes of the latter. The results are given in Table XII.

TABLE XII.

Description of ore.	Weight of sample. G.	Standard used.	Mn present. %.	Mn found. %.
U. S. B. S. No. 28, Norrie Ore....	1.0000	*d*	0.465	0.460
U. S. B. S. No. 29, Magnetite.....	1.0000	*f*	0.07	0.068

In addition some twenty iron ores of known manganese content used as "unknowns" for students, were analyzed by the above procedure. All the common types of iron ore were represented in this series. The results obtained always agreed well with the values given by other methods.

General Procedure.

The material to be analyzed is brought into a solution containing in 100 cc. at least 10–15 cc. concentrated sulfuric, 20 cc. of nitric or 5–10 cc. of syrupy phosphoric acid, or mixtures of two or more acids. The solution should previously have been freed from reducing agents by boiling with nitric acid, adding a little persulfate if carbon compounds are present, as with steel; if chloride is present it should be evaporated with nitric and sulfuric acids to fumes of the latter. 0.2 to 0.4 g. of KIO_4 or $NaIO_4$ is added or an equivalent amount of $Na_3H_2IO_6$, the solution boiled for a minute, kept hot 5 to 10 minutes, cooled, diluted to the proper volume and compared with a standard of known manganese content similarly prepared. When ready for comparison the solution should not contain much more than 1 mg. of manganese per 50 cc., otherwise the color will be too dark.

In the presence of considerable iron, either sulfuric or phosphoric acid must be present, since ferric periodate is insoluble in fairly concentrated nitric acid but readily soluble in the other acids. A very large concentration of acid does no harm in any case, neither does a longer time of heating.

The method is especially adapted for the determination of manganese in water, soil, ores and other materials in which it is present in small amounts. Its application to alloy steels will be made the subject of a special paper.

The expense of the reagent is not prohibitive, since relatively small amounts are required. It is less expensive than sodium bismuthate, which is widely used. Simple methods for the preparation of periodic acid and its salts have been devised and will be discussed in a later paper.[1]

This method has been used by students in this laboratory during the past three years for the determination of small amounts of manganese in steel, iron ore and other minerals, and has been found entirely satisfactory.

Summary.

1. The periodates of the alkali metals are excellent reagents for the oxidation of manganese to the form of permanganate in the colorimetric estimation of this element. The oxidation with a small excess of permanganate is certain and complete, providing sufficient free acid is present to prevent the precipitation of manganic periodates or oxides. This oxidation is more reliable than that with persulfate and silver nitrate, and, unlike this, it gives the true permanganate color.

2. A high concentration of acid, the presence of ammonium salts, and prolonging the time of heating are all without effect. Traces of chloride do not interfere and even larger amounts may be expelled by heating with an excess of the reagent. Of the common metals none interferes, unless it forms a colored ion.

3. The procedure involved is simple; no catalyzer is required, and the solutions may be kept unchanged for months.

4. Relatively large amounts of manganese may be oxidized.

5. Reducing agents must be removed by suitable means, such as treatment with nitric acid. If much iron is present either sulfuric or phosphoric acid must be present to prevent the precipitation of ferric periodate. Phosphoric acid also serves to remove the yellow color of ferric salts. These acids, especially phosphoric, are also more efficient in preventing the precipitation of manganese compounds.

6. Excellent results were obtained by applying this method to analyzed steels and iron ores, and the processes used are described.

7. Attempts to use this as the basis of a volumetric method were unsuccessful.

8. The general procedure is described.

9. A complete bibliography of the colorimetric determination of manganese is appended.

1. W. Crum, *Ann.*, **55**, 219 (1845), suggests the use of PbO_2 in HNO_3 solution but gives no details.

2. Hoppe-Seyler, *J. prakt. Chem.*, **90**, 303 (1863), proves spectroscopically that the color formed by PbO_2 is due to permanganate.

3. P. Pichard, *Compt. rend.*, **75**, 1821 (1872), also Dingler's *Polytech. J.*, **207**, 136 (1873), uses PbO_2 in HNO_3 solution, and gives details of method.

---

[1] At the present time dealers are practically unable to supply these salts, on account of the small demand, but the Eberbach and Son Co., of this city, has kindly consented to undertake their preparation.

4. A. Brunner, Dingler's *Ibid.*, **210**, 278 (1873), forms green manganate by fusion with NaOH.

5. M. Koppmayer, Dingler's *Ibid.*, **211**, 133 (1874), found useless the method described in 4.

6. S. Peters, *Chem. News*, **33**, 35 (1876), uses PbO_2 as oxidizing agent.

7. A. Ledebur, *Berg. hütt. Z.*, **41**, 417 (1882), uses PbO_2.

8. M. Osmond, *Bull. soc. chim.*, **43**, 66 (1885), forms manganic metaphosphate by use of $NaPO_3$ and PbO_2 or ozone in acid solution.

9. Reddrop and Ramage, *J. Chem. Soc.*, **67**, 275 (1895), footnote. The use of sodium bismuthate is suggested.

10. H. Marshall, *Chem. News*, **83**, 76 (1901), suggests for the first time the use of persulfates and $AgNO_3$.

11. H. E. Walters, *Ibid.*, **84**, 239 (1901), uses persulfate and silver,

12. L. Dufty, *Ibid.*, **84**, 248 (1901), gives full directions for the use of sodium bismuthate.

13. Fr. Croner, *Gesundh. Ing.*, **28**, 197 (1905), also *Chem. Zentralb.*, **1905**, II, 74, precipitates Mn in alkaline tartarate solution by adding ferrocyanide.

14. N. Tarugi, *Gazz. chim. ital.*, **36**, I, 332 (1906), oxidizes Mn to colored form in alkaline glycerine solution by air or hypochlorite.

15. Duyk, *Ann. chim. analyt. appl.*, **12**, 465 (1907), oxidizes Mn to $KMnO_4$ in slightly alkaline solution by hypochlorite using $CuSO_4$ as catalyzer.

16. P. Holland, *Chem. News*, **96**, 3 (1907), uses persulfate and silver.

17. Dumitrescu and Nicolau, *Ann. fals.*, **3**, 370, 407 (1910), use persulfate with a drop of $Co(NO_3)_2$.

18. J. Rodenburg, *Chem. Weekblad*, **7**, 877 (1910), uses persulfate and silver.

19. M. R. Schmidt, THIS JOURNAL, **32**, 965 (1910), uses persulfate and silver.

20. O. Prandl and A. Civetta, *Staz. sper. agrar. ital.*, **44**, 58 (1911), use PbO_2.

21. G. Bertrand, *Bull. soc. chim.*, [4] **9**, 361 (1911), uses persulfate and silver.

22. R. O. Gortner and C. O. Rost, *J. Ind. Eng. Chem.*, **4**, 522 (1912), use sodium bismuthate and indicate objections to persulfate.

23. M. Dittrich, *Zeit. anorg. allgem. Chem.*, **80**, 171 (1913), uses persulfate and silver.

24. The Chemist's Committee of the U. S. Steel Corporation, *J. Ind. Eng. Chem.*, **4**, 807 (1912), uses persulfate and silver.

25. F. Haas, *Z. Nahr. Genussm.*, **25**, 392 (1912), uses persulfate and silver.

26. E. Schowalter, *Ibid.*, **26**, 104 (1913), uses persulfate and silver.

27. L. Hartwig and H. Schellbach, *Ibid.*, **26**, 439 (1913), use persulfate and silver.

28. H. Lührig, *Chem. Ztg.*, **38**, 781 (1913), uses persulfate and silver.

29. J. Tillmans and H. Mildner, *J. Gasbel.*, **57**, 496, 523, 544, use persulfate and silver; suggest as a qualitative test adding KIO_4, acetic acid and "tetramethyl base" blue color indicates Mn.

30. Béla von Horváth, *Z. analyt. Chem.*, **53**, 581 (1914), uses persulfate and silver.

31. J. F. Sacher, *Chem. Ztg.*, **39**, 319 (1915), adds NaOH, lets $Mn(OH)_2$ oxidize in air and adds oxalic acid. Red color is due to a double salt.

32. F. Bardach, *Ibid.*, **39**, 457 (1915). Discussion of delicacy of test and reaction involved.

33. J. F. Sacher, *Ibid.*, **39**, 458 (1915). Discussion of delicacy of test and reaction involved.

34. L. Dobbin, *Chem. News*, **113**, 133 (1916). Historical review of persulfate and PbO_2 methods.

ANN ARBOR, MICH.