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Manganese
S. D. S. College

LB 2382
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**AN INVESTIGATION INTO THE BROMATE
METHOD OF MANGANESE DETERMINATION**

A THESIS,
presented in partial fulfillment
of requirements for the degree of
MASTER OF SCIENCE
from South Dakota State College
prepared by
Ray A. Bunday

I. Introduction.

Throughout the history of research in the science of Chemistry the problem of the quantitative determination of manganese has always been a perplexing one. The results have usually fallen short of the theoretical value and this has necessitated the application of an empirical factor(1) which is always undesirable to the true research scientist, if not to the commercial analyst.

Kolthoff and Sandell have made a comprehensive study of the various methods given in the literature for the precipitation of manganese as dioxide and the subsequent volumetric determination of this manganese dioxide. Their study includes the writings of such scientists as Von Knorre, Beilstein and Jawein, Hampe, Blum, Ludert and others.(1)

The writer has referred to Mellor's comprehensive work in inorganic chemistry(2) for the method of preparation of the reagent manganous salt in order to make a suitable solution with which to check the method of analysis chosen for a research problem. Among the scientific writers recorded here are J. I. Watts, J. H. Krepelka and B. Réjha, and J. G. F. Druce. Various authors of textbooks shall be cited later to substantiate certain reactions and methods involved.

With the growing use of manganese in the present day steel industry it has become imperative that better methods for manganese analysis in ores as well as in steel samples be perfected if possible. It is the object of this thesis to investigate further one of these methods which has shown promise of being perhaps more satisfactory than some of the others.

In general, there are two types of methods for the precipitation of manganese dioxide. One involves precipitation in a neutral or alkaline medium by means of bromine, hypobromite, chlorine, hypochlorite, or ferricyanide. The

(1) Kolthoff & Sandell: *Ind. & Engineering Chemistry, Analytical Edition*, 1, 181, (1929)

(2) Mellor: *Inorganic Chemistry*, 12, 402

second type involves precipitation in an acid medium by use of some oxidizing agent such as ammonium or potassium persulfate, sodium bismuthate, potassium chlorate, potassium bromate, or others. Kolthoff and Sandell have dismissed the methods in neutral or alkaline media as being unsatisfactory, especially in the presence of iron.(1)

Briefly, the persulfate method involves the precipitation of manganese dioxide from the solution of a manganous salt in acid (usually sulfuric) solution. The precipitated dioxide is collected by filtration, washed, and dissolved in some reducing agent such as ferrous sulfate or hydrogen peroxide, and the excess reducing agent titrated with permanganate. The disadvantage of this method lies in the ready decomposability of the persulfate.(1)

The bismuthate method is based on the fact that a manganous salt, in the presence of nitric acid, is oxidized to permanganic acid by sodium bismuthate. To the cold manganous solution acidified with nitric acid, a slight excess of sodium bismuthate is added. After agitation, the excess bismuthate is removed by filtration through asbestos and washed with 3% solution of nitric acid. An excess of standard ferrous sulfate solution is added and titrated at once with permanganate.(3) The solution must be kept cold in this method and the nitric acid used must be free from nitrous acid.

The chlorate method, sometimes called the Williams method, ((3) p. 563) depends upon the precipitation of manganese dioxide by boiling the manganous solution with concentrated nitric acid and potassium chlorate. The precipitate is dissolved in an acid and a known quantity of reducing agent, usually acid ferrous sulfate or ferrous ammonium sulfate, added. The excess reducing agent is then titrated with potassium permanganate. These reducing agents oxidize readily and must be titrated against the permanganate at least every day in order to obtain their accurate normalities.

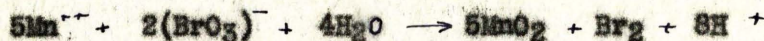
(3) Treadwell-Hall: Quantitative Analysis, 2, 568, (1935)

In general the amount of manganese dioxide produced may also be determined iodometrically if desired. This method involves the addition of an acidified portion of potassium fluoride solution together with a small excess of potassium iodide. The liberated iodine is then titrated with standard sodium thiosulfate solution.(1)

The particular method chosen for further investigation was the bromate method because potassium bromate is not easily decomposed by boiling in dilute acid solutions.(1) Hampe found that potassium bromate could be used in place of the chlorate, but preferred the chlorate.(1) The bromate method seems particularly applicable where relatively large quantities of manganese are determined, especially in the presence of other compounds, notably compounds of iron and zinc. There seems to be one outstanding disadvantage in the bromate method, however, in the fact that determinations in the absence of iron and zinc are in many cases three to 5 per cent below the theoretical value. This is roughly about twice the percentage, below the theoretical value, found in determinations where iron and zinc compounds were present. Consequently, to investigate this discrepancy further, we have selected for analysis manganese solutions that are as chemically pure as they can be conveniently made by using the analytical reagent and distilled water.

II. Theoretical Development.

Manganous salts are oxidized to manganese dioxide by boiling a short time with potassium bromate in dilute acid solution according to the following equation; (1)



The reaction is analagous to the oxidizing action of the chlorates and the iodates, wherein the halogen is eventually liberated and the valence of the oxidized element raised.

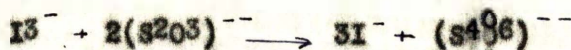
When manganese dioxide and ferrous sulfate are brought together in the presence of an acid, say sulfuric, because sulfuric acid is often used in standard ferrous sulfate to keep it stable, the Mn^{++} is reduced and the Fe^{++} is oxidized according to the equation;



This is the basis for the determination of the amount of manganese dioxide formed. As it is necessary to add an excess of ferrous sulfate solution, that excess must be determined by titration with some suitable reagent. One of the most common of these is potassium permanganate. This reacts with ferrous sulfate in the presence of sulfuric acid and the Fe^{++} is oxidized to Fe^{+++} . In turn the $(\text{MnO}_4)^-$ is reduced to Mn^{++} according to the equation; (4)



Should it become desirable to determine the manganese dioxide by the iodometric method, the iodine, liberated by the treatment of manganese dioxide with potassium iodide in the presence of an acid, is titrated with standard sodium thiosulfate using soluble starch as an indicator. (5) The essential equation involved is;



- (4) Baber, Estabrooke, Lehrman; Elements of General Chemistry, 525 (1931)
 (5) Latimer and Hildebrand; Reference Book of Inorganic Chemistry, 141 (1929)

III. Materials and Apparatus.

The potassium bromate used was the Mallinkrodt's analytical reagent. In two of the manganous sulfate solutions made the Baker's Analyzed tetrahydrate salt was used, and in another Mallinkrodt's Analytical Reagent.

Three separate 1-liter portions of manganous sulfate solution were made during the series of determinations. The first was made up from the Baker's Analyzed tetrahydrate salt gravimetrically, but its use was dispensed with early on further investigation of the many possible hydrates of the salt.

The second solution was made by heating the Baker's Analyzed tetrahydrate in a porcelain crucible to a dull redness over a Bunsen burner for approximately one-half hour. The burner was frequently removed so as not to overheat the contents. The authority consulted in this respect was Mellor whom I shall quote in part: "When hydrated manganous sulfate is heated to redness it forms the anhydrous salt. J. I. Watts found that the anhydrous salt is formed when the hydrate is heated to 280° . J. H. Krepelka and B. Rejha found that the salt is anhydrous at 450° ; and J. G. F. Druce obtained the anhydrous salt by heating the hydrate in nitrobenzene boiling at 207° ; but not in xylene boiling at 140° ."(2) After cooling in a desiccator, 2.7487 grams were carefully weighed and dissolved in 1 liter of distilled water at a temperature of 20° . Great care was taken when the portions were later pipetted out of this solution that the temperature was kept as close to 20° as possible.

The third solution was made by heating the Mallinkrodt's Analytical Reagent tetrahydrate for a period of four hours in an electric oven controlled by a rheostat so that the temperature did not exceed 340° Fahrenheit. The same procedure was followed thereafter as in the case of the second solution.

In preparation of the standard potassium permanganate solution, sufficient of the Mallinkrodt's Analytical Reagent was weighed out to make up about $2\frac{1}{2}$ liters of approximately .05 normal solution. (This was approximately .05 x 2.5 x formula wt. of $KMnO_4$), inasmuch as manganese here in reacting undergoes a valence

5

change of 5) After dissolving the weighed portion of salt in a beaker sufficiently large, this solution was heated and boiled for at least fifteen minutes and allowed to stand over night. It was then filtered through asbestos, formerly treated with some oxidizing reagent so as to remove all organic impurities. ((3) p. 102) A Buchner funnel with filter flask was used for this purpose and the first 25 cc. of solution discharged through the funnel was discarded. The filter flask was then washed out with more of the filtered solution and then the reagent bottle of 2 or more liters capacity washed out likewise. As the filtration into the filter flask proceeded, transfers of the solution were made as necessary from filter flask to reagent bottle.

The permanganate solution was then standardized by the oxalate method in the following manner: Sufficient C.P. sodium oxalate was weighed out to react with approximately 30 cc. of the potassium permanganate solution. This oxalate was dissolved in about 50 cc. of distilled water and 15 cc. of 4 normal sulfuric acid were added. The mixture was then heated to 75° - 85° and titrated while still hot with the permanganate solution, very slowly at first and then faster as the titration proceeded. ((3) pp. 102-103) The reaction was according to the equation:



For the preparation of the ferrous sulfate solution, a sufficient quantity of the Mallinkrodt's Analytical Reagent heptahydrate salt was weighed out to make up about $2\frac{1}{2}$ liters of approximately .05 normal solution. (This was approximately $.05 \times 2.5 \times \frac{1}{\text{formula wt. of FeSO}_4 \cdot 7\text{H}_2\text{O}}$ inasmuch as iron here in reacting undergoes a valence change of 1) Enough distilled water was added to the salt to dissolve it, and the solution transferred to a clean reagent bottle. About 100 cc. of concentrated sulfuric acid were added to assure reasonable stability and more distilled water was added to bring up to the required volume. (3) Due to a mistake the first ferrous sulfate solution made up was only about one-half the desired normality, but it was used in two determinations, nevertheless. Afterwards a solution approximately .05 normal was made up and used.

The ferrous sulfate solution was titrated with the potassium permanganate solution and the volumetric equivalent of ferrous sulfate solution per unit volume of potassium permanganate thereby determined. It is interesting to note that the ferrous sulfate gradually declined in normality. More especially noticeable was this decline during the extremely warm summer season at temperatures close to 30°C. This necessitated a check of the ferrous sulfate solution against the permanganate solution at least every alternate day during the warm season.

In order to assure sufficient accuracy in the volumetric determinations involved, it was necessary to calibrate the burettes and pipettes used. The 50 cc. burettes used were calibrated in the following manner: The burette was mounted in holder and filled with distilled water. The temperature of the water was carefully taken and the volume brought to the zero mark. The burette was drained down to the 10 cc. mark into a small bottle previously weighed to an accuracy of 1 centigram. Bottle and contents were weighed as quickly as possible to the nearest centigram. The burette was then drained down to the 20 cc. mark into the same bottle with former contents and weighed as before. This process was repeated until weights had been taken for each of the five 10 cc. portions of water in the burette. When the small bottle used for weighing became filled, it was emptied, weighed to the nearest centigram, and the process was continued. Burettes were chosen with the graduation lines indicating integral cc.'s extending all the way around the tube. The tenth-cc. markings also extended the greater portion of the distance around the tube. This is of great assistance to the operator in enabling him to keep his eye on the proper level while reading the burette.

Two 50 cc. burettes were calibrated in the above manner and the tables for those calibrations are herewith shown: (See tables on next page.)

Burette No. 1		Temperature of Water--21°- 22°		
Burette Reading cc.	Wt. Water grams	Vol. Water cc. *	Error cc.	Total Error cc.
0 - 10	9.91	9.93	-.07	-.07
10 - 20	9.90	9.92	-.08	-.15
20 - 30	10.01	10.03	+.03	-.12
30 - 40	9.98	10.00	.00	-.12
40 - 50	10.00	10.02	+.02	-.10
0 - 10	9.92	9.94	-.06	-.06
10 - 20	9.91	9.93	-.07	-.13
20 - 30	10.02	10.04	+.04	-.09
30 - 40	9.97	9.99	-.01	-.10
40 - 50	10.00	10.02	+.02	-.08
0 - 10	9.91	9.93	-.07	-.07
10 - 20	9.92	9.94	-.06	-.13
20 - 30	10.02	10.04	+.04	-.09
30 - 40	9.98	10.00	.00	-.09
40 - 50	10.01	10.03	+.03	-.06
0 - 10	9.89	9.91	-.09	-.09
10 - 20	9.93	9.95	-.05	-.14
20 - 30	10.01	10.03	+.03	-.11
30 - 40	9.97	9.99	-.01	-.12
40 - 50	10.02	10.04	+.04	-.08

Burette No. 2		Temperature of Water--24°		
Burette Reading cc.	Wt. Water grams	Vol. Water cc. *	Error cc.	Total Error cc.
0 - 10	9.96	9.99	-.01	-.01
10 - 20	9.92	9.95	-.05	-.06
20 - 30	10.00	10.03	+.03	-.03
30 - 40	9.99	10.02	+.02	-.01
40 - 50	10.03	10.06	+.06	+.05
0 - 10	9.97	10.00	.00	.00
10 - 20	9.92	9.95	-.05	-.05
20 - 30	10.00	10.03	+.03	-.02
30 - 40	10.00	10.03	+.03	+.01
40 - 50	10.02	10.05	+.05	+.06

* (6) Hodgman and Lange: Handbook of Chemistry and Physics, 859, (1931)

In order to facilitate the process of making corrections in burette readings, a graph for each burette was made showing the average total error according to the table.

Pipettes used were calibrated in the following manner: A beaker was filled with distilled water and the temperature of the water carefully taken. The pipette was cleaned in cleaning solution and carefully rinsed in distilled water. Then one or two portions of water from the beaker were drawn up into the pipette and discharged. The pipette was then filled to the mark and drained into the weighing bottle as in the case of the burettes, and the weight quickly taken to the nearest centigram. The results of the calibrations are shown herewith in the tables:

Pipette No. 1	To deliver	Temperature of water 25°
Fipette Reading cc.	Wt. Water grams	Vol. Water cc. *
10	9.89	9.92
10	9.87	9.90
10	9.89	9.92
10	9.89	9.92
10	9.87	9.90
10	9.88	9.91
10	9.89	9.92
10	9.88	9.91
10	9.88	9.91
10	9.87	9.90

Therefore the average
delivery of Pipette
No. 1 is 9.91 cc.

Pipette No. 2	To deliver	Temperature of water 24°
10	9.88	9.91
10	9.86	9.89
10	9.87	9.90
10	9.84	9.87
10	9.87	9.90
10	9.88	9.91
10	9.88	9.91

Therefore the average
delivery of Pipette
No. 2 is 9.91 cc.

(cont. on next page)

Pipette No. 2 (cont.) To deliver		Temperature of water 24°
Pipette Reading cc.	Wt. Water grams	Vol. Water cc. *
10	9.87	9.90
10	9.90	9.93
10	9.88	9.91
10	9.89	9.92
10	9.89	9.92
10	9.88	9.91
10	9.89	9.92
10	9.90	9.93

Other pipettes of different capacities were also used in the series of determinations, but they had been previously calibrated and a repetition of the process was not necessary.

* (6) Hodgman and Lange: Handbook of Chemistry and Physics, 839, (1931)

IV. Experimental.

Several determinations were made in quadruplicate during the summer of 1935, but the results of these are not recorded because of their inaccuracy. It seems that the manipulation requires a certain amount of practice before reasonable efficiency can be attained. In addition to this, as before mentioned, the manganous sulfate solution used was made up gravimetrically directly from the tetrahydrate without attempting to convert the salt to the anhydrous condition.

The general method used follows; A solution of a manganous salt, preferably the sulfate, standardized gravimetrically, is made up. Portions of this solution are pipetted into a 500 cc. Erlenmeyer flask. Enough 6 normal sulfuric acid is added to assure a normality of .5 to 1 in the medium where the precipitation takes place. Distilled water is added to bring the total volume of liquid in the flask to the desired amount. (Kolthoff and Sandell varied to a limited extent these total volumes even with identical portions of manganous salt solution) A weighed portion of solid potassium bromate, greatly in excess of the theoretical amount necessary to react, is added, and the whole is boiled for a definite time, the water lost by evaporation being replaced from time to time as needed to keep the total volume in the flask reasonably constant. (Kolthoff and Sandell also varied this time of boiling and decided that five minutes were sufficient) After allowing to cool sufficiently for handling, the precipitate is filtered through quantitative filter paper and washed with hot water until free from bromate. Presence of a bromate is determined by the appearance of a brownish color when a few drops of the filtrate are added to a solution of potassium iodide acidified with sulfuric acid. Filter paper and its contents are now transferred back to the original flask and an excess of standard ferrous sulfate solution added from either a calibrated burette or pipette. Considerable difficulty is sometimes experienced here in getting all the manganese dioxide to readily react and dissolve. When all the manganese

dioxide is dissolved, the excess ferrous sulfate solution is titrated with a standard potassium permanganate solution from a calibrated burette. It is highly desirable to have the ferrous sulfate and potassium permanganate solutions of very near the same normality.

After substantially following out the above method in quadruplicate on portions of manganous sulfate containing approximately .01 gram of manganese each, and obtaining results that were dubiously successful, several innovations to the method were suggested. They were not suggested simultaneously, but were evolved as the determinations progressed, in the hope that something might be uncovered to make the method more accurate.

It was suggested at first to use boiling periods of one hour in order to give plenty of time for the oxidation of the manganous salt. Later trials were made using much less time for boiling. Then the suggestion was made that the filtrate be treated with another like portion of potassium bromate and the operation be repeated in the hope that possibly more manganese dioxide would be precipitated in this second oxidation.

When a long period of boiling with the bromate was used, it was found that in many cases the filtrate was colored with permanganate formed as the result of further oxidation of the compounds of manganese present. An attempt was made to determine colorimetrically the amount of manganese in the colored filtrates, but this determination could be essentially only very approximate, owing to the fact that the cast of color in the filtrate was different from that in distilled water with small portions of standard potassium permanganate solution added thereto. After experiencing such difficulty in this undesired further oxidation to permanganates, it was suggested that, at the beginning of the second oxidation, before the additional portion of potassium bromate was added, that a small portion of sodium bisulfite, say .6 to .8 gram, be added in the hope that the permanganate present would be first reduced to a manganous salt and then oxidized to manganese dioxide by the bromate. Some additional manganese dioxide was obtained in this manner as shall be seen by the recorded results later.

Considerable variability in the coloration of the filtrates by permanganate was evident, even in the same apparent treatment of identical samples. Sometimes this color disappeared entirely upon filtration, thus giving rise to the speculation that the filter paper reacts substantially with the permanganate. This prompted several blank determinations of the effect of the filter paper on the standard potassium permanganate used. These determinations were carried out under conditions approaching as nearly as practicable those encountered in practice.

To recapitulate then, our innovations to the method of Kolthoff and Sandell include (1) the second oxidation, i.e., the treatment of the filtrate from the original oxidation with a second portion of potassium bromate and the repetition of the oxidizing process, (2) the addition of sodium bisulfite prior to the addition of the bromate in a number of these second oxidations, and (3) the attempt to determine quantitatively the effect of the filter paper on the standard potassium permanganate solution used.

Inasmuch as revisions and innovations were added to the method from time to time in the hope of improving it, it has been decided to tabulate the determinations in the order of their performance. Such explanatory material as seems necessary to a thorough understanding of the procedure shall be interspersed among the tables.

Three conditions were uniform throughout all the determinations, so they shall be mentioned at the beginning to avoid needless repetition. In each determination, regardless of the amount of manganous sulfate taken, portions of potassium bromate weighing 1.5 grams were used. 10 cc. of 6 normal sulfuric acid in a total volume of 100 cc. also constituted the medium in which the oxidation took place.

The first determination in quadruplicate is recorded in Table I. Here the boiling period for each oxidation was one hour. The filter paper used was Munktell quantitative No. 3. No attempt was made to determine colorimetrically the amount, if any, of permanganate in the filtrates. Neither was there any attempt to take into account the action of potassium permanganate on the filter

paper. Sodium bisulfite was used prior to the second oxidation. Other conditions are mentioned in the table.

TABLE I

(Normality of $KMnO_4$ solution = .0504)

(1 cc. $KMnO_4$ solution $\bar{1}$.9353 cc. $FeSO_4$ solution)

First Oxidation Second Oxidation

No.	gm. Mn taken	cc. $FeSO_4$ used	gm. Mn found	cc. $FeSO_4$ used	gm. Mn found	total gm. Mn found	Error gm.	Error %
1	.010	13.35	.00948	1.65	.00075	.01023	+.00023	+2.3
2	.010	13.99	.00993	1.06	.00075	.01068	+.00068	+6.8
3	.010	13.14	.00933	.64	.00045	.00978	-.00022	-2.2
4	.010	13.22	.00939	.76	.00054	.00993	-.00007	-.7

The second determination was made under conditions exactly the same as those of the first. The results of this determination follow:

TABLE II

1	.010	spoiled	-----	-----	-----	-----	-----	-----
2	.010	13.65	.00970	.82	.00058	.01028	+.00028	+2.8
3	.010	13.56	.00963	2.00*	.00142	.01105	+.00105	+10.5
4	.010	13.35	.00948	2.48*	.00176	.01124	+.00124	+12.4

The third determination was made under conditions the same as mentioned in Tables I and II, with the exception that a different standardized solution of ferrous sulfate was used. This solution was very close in normality to that of the potassium permanganate solution used.

* Obvious Errors

TABLE III

(1 cc. KMnO_4 solution = .9477 cc. FeSO_4 solution)

No.	First Oxidation			Second Oxidation			Error gm.	Error %
	gm. Mn taken	cc. FeSO_4 used	gm. Mn found	cc. FeSO_4 used	gm. Mn found	total gm.Mn found		
1	.010	6.62	.00967	.29	.00042	.01009	+.00009	+ .9
2	.010	6.49	.00948	.52	.00076	.01024	+.00024	+ 2.4
3	.010	6.64	.00969	.48	.00070	.01039	+.00039	+ 3.9
4	.010	6.49	.00948	.00*	.00000	.00948	-.00052	-5.2

The fourth determination was made under conditions the same as in Table III, with the exception that the normality of the ferrous sulfate solution had changed in the meantime.

TABLE IV

(1 cc. KMnO_4 solution = .952 cc. FeSO_4 solution)

1	.010	6.41	.00930	.08	.00012	.00942	-.00058	-5.8
2	.010	6.60	.00957	.33	.00048	.01005	+.00005	+ .5
3	.010	6.43	.00932	.14	.00020	.00952	-.00048	- 4.8
4	.010	6.45	.00935	.05	.00007	.00942	-.00058	-5.8

It will be noted in Tables I, II, III, and IV that there are several cases where the total manganese found exceeds the theoretical amount by large per cent. It will also be noted that this error creeps in because of some difficulty connected with the second oxidation.

As has been before mentioned, the behavior of the permanganate-colored filtrates prompted a check as to the effect of the filter paper on the standard potassium permanganate solution used. The first one of these checks was, in all probability, not as accurate as later ones made under conditions more closely simulating the conditions encountered in practice, but the results were incorporated in Tables V and VI, and the details of the determination are included herewith: 90 cc. of distilled water were placed in an Erlenmeyer flask and the

*Occasionally the permanganate used to titrate the excess ferrous sulfate, when that excess is small, calculates as the equivalent of a greater volume of ferrous

9 cm. Whatman No. 40 filter paper (the type used in all subsequent determinations) was torn into pieces approximately 2 cm. square and placed in the flask. The pieces were stirred in the water and somewhat disintegrated with a glass rod. Standard ferrous sulfate solution was now added from a pipette, allowed to stand 15 minutes, and then titrated with standard potassium permanganate solution. The results of this determination are tabulated:

(1 cc. KMnO_4 solution = 1 cc. FeSO_4 solution)

No.	cc. FeSO_4 used	cc. KMnO_4 used
1	9.91	9.95
2	9.91	9.97
3	9.91	9.94
4	9.91	9.90

Therefore the average number of cc. of potassium permanganate solution needed to react with the filter paper in titration under the above conditions is .03 cc. This is the equivalent of .03 cc. ferrous sulfate solution.

Heretofore, no particular attention had been paid to the apportionment of time between the various operations in the method. When, for instance, the manganese dioxide was precipitated and the excess ferrous sulfate added, it was sometimes deemed a timely procedure to let it stand for a few hours or even over night prior to titrating with the permanganate. As has already been mentioned, considerable difficulty was experienced in getting all the manganese dioxide to dissolve, and the wait at this juncture seemed justifiable enough. Whether or not this practice was justified may be answered by a comparison of the results in Tables V and VI.

In Table V, the manganese dioxide with filter paper recovered from the first oxidation was allowed to stand over night with an excess of ferrous sulfate solution. In Table VI, the titration with potassium permanganate was made

(cont. from page 15) sulfate that that actually used to dissolve the manganese dioxide. This must be due, either to mechanical error or to the reaction of potassium permanganate with reactable materials used in the determination. Obviously we can not put down a negative reading of ferrous sulfate used here, so we record it as zero.

just as quickly as the manganese dioxide could be dissolved. All other conditions were the same* with the exception of the change in brand of filter paper and the slight change in normality of the ferrous sulfate solution.

TABLE V

(1 cc. FeSO_4 solution = 1 cc. KMnO_4 solution)

No.	First Oxidation			Second Oxidation			total gm.Mn found	Error gm.	Error %	
	gm. Mn taken	cc. FeSO_4 used	cc. FeSO_4 blank	gm. Mn found	cc. FeSO_4 used	cc. FeSO_4 blank				gm. Mn found
1	.00991	9.17	.05	.01260	.43	.03	.00063	.01323	+.00332	+33.5
2	.00991	9.37	.03	.01288	.19	.03	.00028	.01316	+.00325	+32.8
3	.00991	9.12	.03	.01254	.11	.03	.00019	.01273	+.00282	+28.5
4	.00991	8.94	.03	.01229	.36	.03	.00053	.01282	+.00291	+29.4

The results in Table V are ridiculously high in their inaccuracy and the only reason the table was given was to compare it with Table VI, where the procedure was subjected to the modification mentioned above.

TABLE VI

1	.00991	6.99	.03	.00962	.37	.03	.00055	.01017	+.00026	+2.6
2	.00991	6.84	.03	.00941	.18	.03	.00029	.00970	-.00021	-2.1
3	.00991	6.87	.03	.00945	.21	.03	.00033	.00978	-.00013	-1.3
4	.00991	6.86	.03	.00944	.19	.03	.00030	.00974	-.00017	-1.7

It will be seen that the results in Table VI are the most accurate, as a group, of any yet recorded. It would seem that such great improvement in results in Table VI over those in Table V should be conclusive enough to forbid the practice of waiting any longer to titrate with permanganate that absolutely necessary after the manganese dioxide has dissolved.

* It might also be mentioned that the determinations from Table V on were made during the summer, whereas the first four determinations recorded were made during the winter and spring.

After further consideration, it was decided to make some further determinations as to the effect of the filter paper on the permanganate solution. In the first determination given above, the filter paper did not receive the same treatment that it receives in actual practice. No potassium bromate or 6 normal sulfuric acid were used and the paper was not subjected to washing with hot water to remove the bromate. Neither was sodium bisulfite used as in the case of some of the second oxidations. Accordingly, several determinations were devised to simulate as closely as practicable the conditions the filter paper actually undergoes in practice. These determinations checked so well in quadruplicate that the blanks determined are applied in the calculations involved in all the remaining Tables.

The second filter paper determination was devised to simulate most closely the conditions encountered in the first oxidation. 10 cc. of 6 normal sulfuric acid were added to 90 cc. of water in an Erlenmeyer flask. 1.5 gm. of potassium bromate were added and the whole boiled for 10 minutes. Contents of the flask were discharged through the filter paper and the paper was washed with hot water until free from bromate. Paper was then transferred back to the flask and 2 cc. of the ferrous sulfate solution added from pipette and allowed to stand 2 $\frac{1}{2}$ hours. (Very frequently this much time is used in dissolving the manganese dioxide in practice) Paper was stirred and rubbed with glass rod, as is done in getting the manganese dioxide to dissolve, and the titration with permanganate made. The results follow:

(1 cc. $KMnO_4$ solution = 1.032 cc. $FeSO_4$ solution)

No.	cc. $FeSO_4$ used	cc. $KMnO_4$ used = cc. $FeSO_4$
1	2.00	2.04
2	2.00	2.04
3	2.00	2.06
4	2.00	2.04

Hence, under the above conditions, the filter paper reacts with enough of the permanganate solution to be the equivalent of .11 cc. of the ferrous sulfate solution.

The third filter paper determination was exactly the same in procedure as the second, except that more ferrous sulfate was used, and that the paper stood only 15 to 20 minutes with ferrous sulfate before titration. This procedure was designed to simulate most closely the conditions of the second oxidation when no sodium bisulfite was used.

(1 cc. KMnO_4 solution = 1.032 cc. FeSO_4 solution)

No.	cc. FeSO_4 used	cc. KMnO_4 used = cc. FeSO_4	
1	4.00	4.00	4.13
2	4.00	4.01	4.14
3	4.00	4.03	4.16
4	4.00	4.02	4.15

Hence, the equivalent of the filter paper, under the above conditions, in terms of ferrous sulfate solution is about .14 cc.

The fourth and last filter paper determination was designed to simulate most closely the conditions when sodium bisulfite was used prior to the second oxidation. Its only basic difference, then, from the preceding determination was that .6 to .8 gm. of sodium bisulfite was added to the rest of the ingredients. The boiling period was 25 minutes, and the paper stood approximately 1 hour before titration.

No.	cc. FeSO_4 used	cc. KMnO_4 used = cc. FeSO_4	
1	4.00	3.99	4.12
2	4.00	3.95	4.08
3	4.00	3.97	4.10
4	4.00	3.95	4.08

Hence, the equivalent of the filter paper, under the above conditions, in terms of ferrous sulfate solution is about .09 cc.

In Tables VII and VIII, the conditions under which the determinations were made were somewhat changed. Four samples were used in each quadruplicate determination ranging in quantity of manganese from .002 gm. to nearly .05 gm. There were no other variations from conditions in the former Tables, except, of course, the addition of relatively larger volumes of ferrous sulfate solution where greater

volumes of manganous solution were taken. An effort was also made here to make a colorimetric determination of the manganese in the filtrates. This was done by filling a 100 cc. Nessler jar with the filtrate and, by trial and error, getting it to coincide in depth of color with a sample of equal volume in a like jar, made up of distilled water and a known volume of the standard potassium permanganate solution. (0.1 cc. of the .0504 normal $KMnO_4$ solution is the equivalent of .00005 gm. Mn) As before stated, this comparison was rather difficult owing to the difference in cast of color between the two solutions compared.

TABLE VII

(1 cc. $KMnO_4$ solution = 1 cc. $FeSO_4$ solution)

No.	First Oxidation				Second Oxidation				total gm. Mn found	Error gm.	Error %	
	gm. Mn taken	cc. $FeSO_4$ used	cc. $FeSO_4$ blank	g. Mn BrO_3 oxid.	g. Mn color	cc. $FeSO_4$ used	cc. $FeSO_4$ blank	g. Mn BrO_3 oxid.				g. Mn color.
1	.002	1.20	.11	.00179	.00016	.12	.09	.00029	.00005	.00213	+.00013	+6.5
2	.005	3.25	.11	.00460	.00016	.13	.09	.00030	.00007	.00497	-.00003	-.6
3	.00991	6.67	.11	.00929	.00019	.07	.09	.00022	.00008	.00959	-.00032	-3.2
4	.0497	35.25	.11	.04844	.00000	.00	.09	.00005	.00000	.04849	-.00121	-2.4

TABLE VIII

(1 cc. $KMnO_4$ solution = 1.015 cc. $FeSO_4$ solution)

1	.002	1.12	.11	.00167	.00015	.07	.09	.00022	.00003	.00192		-4.0
2	.005	3.11	.11	.00438	.00016	.07	.09	.00022	.00000	.00460		-8.0
3	.00991	6.57	.11	.00908	.00017	.06	.09	.00020	.00002	.00930		-6.1
4	.04993	35.00	.11	.04775	.00002	.00	.09	.00001	.00000	.04776		-4.3

The results from Tables VII and VIII are not consistent enough to establish anything definitely, but they indicate that the widest range of error seems to be in the determination of samples containing small quantities of manganese.

*Obviously it is only the colorimetric determination in the filtrate after the second oxidation that figures in the final total determination of manganese.

The colorimetric determination in the filtrate after the first oxidation is given, however, as a matter of record.

The smallest range of error is evident in the samples containing the largest quantities of manganese. This confirms the findings of Kolthoff and Sandell in these respects. (1) It will also be seen that there was, in general, more coloration in the filtrates from samples containing small quantities of manganese than from samples containing large quantities. Particular attention should be called to the rather nice gradation in the amount of manganese recovered in the second oxidation. This gradation ranges from relatively large amounts of manganese recovered from the sample containing .002 gm. manganese to practically no manganese recovered from the sample containing .05 gm. manganese.

In Table IX, a new variation was added to the conditions. Samples containing .002 gm. of manganese were taken and boiling periods of 5, 10, 30, and 60 minutes respectively were used on the four samples. The same respective boiling periods were used on each sample during the second oxidation.

TABLE IX

(1 cc. $KMnO_4$ solution = 1.015 cc. $FeSO_4$ solution)

No.	First Oxidation						Second Oxidation						total g. Mn found	Error %
	gm. Mn taken	min. to boil	cc. $FeSO_4$ used	cc. $FeSO_4$ blank	g. Mn BrO_3 oxid.	g. Mn color.	min. to boil	cc. $FeSO_4$ used	cc. $FeSO_4$ blank	g. Mn BrO_3 oxid.	g. Mn color.			
1	.002	5	1.35	.11	.00199	.00000	5	.07	.09	.00022	.00000	.00221	+10.5	
2	.002	10	1.32	.11	.00194	.00001	10	.06	.09	.00004	.00000	.00198	-1.0	
3	.002	30	1.20	.11	.00178	.00003	30	.06	.09	.00000	.00000	.00178	-11.0	
4	.002	60	1.08	.11	.00162	.00010	60	.04	.09	.00018	.00000	.00180	-10.0	

The results in Table IX are very inaccurate, but they again serve to show the unreliability of the method when samples containing small quantities of manganese are used. The boiling time of 10 minutes, however, shows up as very favorable.

Another departure in method, as regards the time of boiling, was taken in Tables X and XI. Samples containing .002 gm. of manganese were used, but the

period of boiling on the first oxidation was varied from zero minutes, i.e., the removal of flask and contents when boiling started, through 1-minute, 3-minute, and 5-minute periods. The period of boiling on the second oxidation was 5 minutes in each case, and no sodium bisulfite was used prior to the second oxidation. Colorimetric determinations of the filtrates were attempted, but they were negative, and so are omitted from the Tables to conserve space.

TABLE X

(1 cc. $KMnO_4$ solution = 1.024 cc. $FeSO_4$ solution)

No.	First Oxidation					Second Oxidation					Error %
	gm. Mn taken	min. to boil	cc. $FeSO_4$ used	cc. $FeSO_4$ blank	g. Mn BrO_3 oxid.	min. to boil	cc. $FeSO_4$ used	cc. $FeSO_4$ blank	g. Mn BrO_3 oxid.	total g. Mn found	
1	.002	0	1.24	.11	.00182	5	.24	.14	.00051	.00233	+16.5
2	.002	1	spoiled	--	-----	-	--	--	-----	-----	-----
3	.002	3	1.25	.11	.00184	5	.00	.14	.00005	.00189	- 5.5
4	.002	5	1.19	.11	.00175	5	.00	.14	.00005	.00180	-10.0

TABLE XI

1	.002	0	1.00	.11	.00150	5	.22	.14	.00049	.00199	- 0.5
2	.002	1	1.00	.11	.00150	5	.66	.14	.00111	.00261	+50.5
3	.002	3	1.09	.11	.00162	5	.45	.14	.00080	.00242	+21.0
4	.002	5	1.33	.11	.00194	5	.00	.14	.00000	.00194	- 3.0

Again the results are unsatisfactory as they have been heretofore in the cases where samples containing small quantities of manganese have been used. As will be seen, the results of the second oxidations in Tables X and XI, without the use of sodium bisulfite, are extremely unsatisfactory.

IV. General Discussion of Results

In regard to the practicability of the second oxidation, it may be said in general, from an analysis of the Tables, that samples containing small quantities of manganese, say .002 gm., yield relatively more manganese on second oxidation than do samples containing larger quantities of manganese. Samples containing approximately .05 gm. of manganese, it is seen, yield practically no manganese on the second oxidation. The difficulty in the second oxidation, it would seem, does not lie so much in precipitating what manganese there is present as manganese dioxide, but in determining such small quantities of manganese. The materials present in the medium seem to react to a certain extent with each other. Unsatisfactory as they are in results, the second oxidations making use of sodium bisulfite are much more uniform and satisfactory in results than those second oxidations where no sodium bisulfite was used.

It seems that boiling periods of 5 to 10 minutes are sufficiently long and even more desirable than periods of one hour. Practically no permanganate color was formed in the liquid media when boiling periods of 5 to 10 minutes were used. When one hour was used, the media were colored considerably with permanganate on the first oxidation. When such a thing takes place, some error is always introduced as this color often fades on filtration.

The filter paper determinations have shown that there is a very definite effect of the paper on permanganate solution. The fading in color of the liquid medium on filtration is an indication of this. It is also indicated in the fading of the permanganate color in sometimes one minute or less on titration. However, the use of more permanganate than theoretically required in titration may not be entirely due to filter paper. If, for instance, ferrous sulfate solution should be, for any reason, oxidized to ferric sulfate while it is in contact with the filter paper and the other ingredients in the medium, less permanganate will be required to titrate the excess ferrous sulfate. This will show, in the calculation, an accordingly greater volume of ferrous sulfate used, and the results for the determination of manganese will be high. As is seen in some

of the Tables, we have some absurdly high results which may be traceable to this very cause.

In order to be more certain as to the effect of filter paper on permanganate solution, an exhaustive study should be made. The paper should be treated under conditions approaching, as nearly as possible, those conditions encountered in practice. Ferrous sulfate, in varying amounts, should be used with the paper in the oxidizing media. Obviously no manganous solution can be used, and consequently the exact conditions of practice can not be simulated. Varied periods of time of standing with ferrous sulfate solution in the media and under different temperatures should be investigated. With this, perhaps, some fairly constant blank for use in calculation could be arrived at.

To overcome the uncertainty of the determinations of manganese by the bromate method, it also seems that an investigation is necessary to determine the effect of the combined ingredients of the oxidizing media on the ferrous sulfate used. Separate portions of ferrous sulfate solution could be titrated with potassium permanganate, and portions of like volume could be introduced into the oxidizing media without filter paper. There they could be allowed to stand for varying periods of time and under various conditions of temperature, and then titration with potassium permanganate solution could be made. Such a procedure would give some indication as to the effect of the oxidizing media alone on the ferrous sulfate solution.

V. Summary

A brief review of the current methods for determination of manganese is outlined and the particular disadvantages of these methods are cited. The method chosen for investigation is discussed briefly and the reactions are explained. Preparation of materials and apparatus as regards the particular problem is noted and the results of the experimental work are tabulated. Discussion as to results and possible improvement in the method is made.

VI. Bibliography

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