equal concentration of bichromate is sufficient to *insure* passivity of the anode and an even smaller ratio is ordinarily effective even at temperatures as high as 150°.

4. The presence of carbonates and bicarbonates in water seems to have no destructive effect on the passivity induced by bichromate.

5. Since chlorides, sulfates and carbonates represent the common salts found in water, the general conclusion of Cushman seems to be verified at least so far as anodic conditions are concerned and the further fact is established that the suggestion of Wyatt (see introduction) is valuable. It seems probable also that since the percentage of chlorides in boiler water is usually small and easily determined that a valuable boiler preservative is provided by the addition of an amount of bichromate forty times that of the chlorides present, calculated as sodium chloride, plus that needed to precipitate the scale-forming factors. The cost of such preservative agent is not excessive. The doubtful factor in this case is the extent of the influence of the anodic current in producing the results above detailed. Experiments are at present under way to determin how long iron will remain unrusted in such inhibitive solutions in the absence of electrical current.

The work above detailed was rendered possible through the C. M. Warren Fund.

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DETERMINATION OF MANGANESE AS SULFATE AND BY THE SODIUM BISMUTHATE METHOD.[1]

BY WILLIAM BLUM.

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CONTENTS.

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[1] Published by permission of the Director of the Bureau of Standards.

I. Introduction.

1. *Importance of Accurate Manganese Determinations.*—In spite of the large number of methods in use for the determination of this important element, results by different methods and chemists seldom show satisfactory agreement. While differences of as much as a few per cent of the manganese present have little commercial significance in iron and steel containing 1% or less of manganese, the highest possible accuracy is demanded in the analysis of high grade materials such as manganese ore and ferro-manganese, of which large amounts enter into commerce, at prices dependent upon the results of analysis. For example, imports of manganese ore by this country in 1911 amounted to 176,852 long tons, valued at $1,186,791. It can readily be seen that a constant error of 1% in the analysis of such material may cause a considerable difference in the total amount paid for the ores. That constant errors of such magnitude are possible with our present methods will be shown in this paper.

2. *Sources of Error in Gravimetric Methods.*—Even with the greatest care, the gravimetric results are not necessarily accurate, due not alone to the possibilities of losses by solubility of precipitates and of too high weight due to contamination from vessels or reagents, but also to uncertainty in the composition of the precipitates as weighed. The three forms in which manganese is most commonly determined gravimetrically are Mn_3O_4, $Mn_2P_2O_7$ and $MnSO_4$. It is generally admitted that the first of these is unsatisfactory, as the composition depends directly upon the temperature of the ignition and the nature of the atmosphere surrounding the precipitate. Even under carefully regulated conditions Raikow and Tischkow[1] could not obtain results which agreed to better than one part in two hundred. Gooch and Austin[2] have shown that the composition of manganese "pyrophosphate" depends upon the content of ammonium salts and ammonia and the temperature, volume and method of precipitation of the manganese ammonium phosphate. Even under the conditions which they recommend, their errors amounted in some cases to 1% of the manganese present, and were in general too high. The method cannot, therefore, be considered satisfactory for highly accurate work, and certainly not for obtaining a known amount of manganese to serve as a primary standard. Experiments described in this paper have led to the conclusion that manganous sulfate, obtained under proper conditions, is the most accurate form in which this element can be weighed, both in gravimetric analysis and in securing a known amount of manganese.

3. *Sources of Error in Volumetric Methods.*—The difficulty of securing a known amount of manganese to serve as a primary standard has hin-

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[1] *Chem. Ztg.*, 35, 1013 (1911).

[2] *Am. J. Sci.*, 6, 233 (1898).

dered the accurate investigation of the great number of volumetric methods which have been proposed. In most cases they have been tested by comparison with other methods, gravimetric or volumetric, which had not been shown to be intrinsically accurate. This fact, together with the usual dependence of the results of such methods upon the precise conditions of operation, has led to the publication of a large number of contradictory papers upon these methods. For example, the Volhard method with its various modifications has been the subject of over fifty investigations since its publication in 1879. It is generally admitted that the results by this method are low unless an empirical factor dependent upon the conditions of operation, is employed, though some investigators have obtained theoretical results under certain conditions. In view of the above situation, it is highly desirable to find some method which will yield results of known accuracy, which are not closely dependent upon the exact conditions of operation, and which may serve to test other methods.

II. The Bismuthate Method.

1. *Outline of Method.*—Of various methods considered, the bismuthate appeared most promising, and has been found to entirely fulfil the above requirements. In this method the manganese in nitric acid solution is oxidized with sodium bismuthate, of which the excess is removed by filtration through asbestos. To the resulting permanganic acid is added a measured excess of ferrous sulfate solution, which is then titrated with permanganate of known strength and of known ratio to the ferrous solution. The investigation therefore resolved itself into a study of the methods of standardizing the permanganate employed in the final titration and the influence of the various conditions of operation upon the results obtained by the bismuthate method.

2. *History of Method.*—The method as originally proposed by Schneider[1] depended upon the use of bismuth tetroxide as the oxidizing agent and titration of the permanganic acid with hydrogen peroxide. In this form the method was employed by Campredon,[2] Mignot[3] and Jaboulay.[4] Reddrop and Ramage[5] modified it by employing sodium bismuthate, which was more readily obtained free from chlorine, and suggested filtration of the permanganic acid directly into the hydrogen peroxide. On account of the instability of the latter reagent Ibbotson and Brearley[6] replaced it by ferrous ammonium sulfate, in which form the method has

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[1] *Ding. poly. J.*, **269**, 224.

[2] *Rev. chim. indust.*, **9**, 306 (1898).

[3] *Ann. chim. anal.*, **5**, 172 (1900).

[4] *Rev. gén. chim.*, **6**, 119 (1903).

[5] *J. Chem. Soc.*, **67**, 268 (1895).

[6] *Chem. News*, **84**, 247 (1901)

been since used, being described in detail by Blair,[1] whose directions for this method are generally followed in this country.

3. *Standardization of Solution.* (*a*) *Discussion of Methods.*—As above stated, the accuracy of any such volumetric method depends principally upon the method of standardization employed. Blair[2] mentions in his book three methods, *viz.*, (*a*) calculation from the iron value, (*b*) use of a steel of known content, and (*c*) use of a known amount of manganous sulfate, without expressing any preference or opinions as to their relative accuracy. Standardization by means of sodium oxalate may be included under (*a*), since values found with this standard under proper conditions[3] have been found at this Bureau to agree with iron values within one part in a thousand.[4] Method (*b*) is a secondary method and is evidently unsuitable for work of high accuracy. As will be shown later, the standardization of manganous sulfate is a tedious operation and subject to considerable errors. For this reason sodium oxalate was considered at this Bureau to be the most convenient and accurate standard for this method. Brinton,[5] however, stated that there was a difference of 1% (at first stated as over 3%) between the values based upon sodium oxalate and manganese sulfate, respectively. In a paper from this bureau by Dr. W. F. Hillebrand and the author[6] the reasons for our belief in the accuracy of the sodium oxalate standard were expressed in the form of a preliminary paper, the conclusions of which have been verified by subsequent investigations described in this paper.

(*b*) *Evidence Based on Reduction and Reoxidation.*—The original basis of our use of the sodium oxalate standard for this method was the fact that if a definit amount of a permanganate solution be reduced and then reoxidized by means of bismuthate, it is exactly equivalent in oxidizing power to the original permanganate. This experiment was based upon a similar one suggested by Wolff[7] and employed by de Koninck[8] for testing the accuracy of the Volhard method for manganese. Its significance as applied to the bismuthate method is that the manganese is oxidized to the same state of oxidation as was originally present in the permanganate, theoretically Mn^{VII}. In the absence of evidence to the contrary it seems highly improbable that any appreciable manganese

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[1] THIS JOURNAL, **26**, 793 (1904), and "Chemical Analysis of Iron," 6th and 7th ed.

[2] In the appendix of the 1912 edition, p. 330, Blair recommends the standardization with sodium oxalate, under approximately the conditions given by McBride, as the most accurate method; a conclusion based upon the work described in this paper.

[3] McBride. THIS JOURNAL, **34**, 415 (1912).

[4] See Bureau of Standards Certificate for Sibley Iron Ore, Standard Sample 27.

[5] *J. Ind. Eng. Chem.*, **3**, 237, 376 (1911).

[6] *Ibid.*, **3**, 374 (1911).

[7] *Stahl u. Eisen*, **11**, 373 (1891).

[8] *Bull. soc. chim. Belg.*, **18**, 56 (1904).

can be present in a filtered permanganate solution in a form other than Mn^{VII}, and still less probable that in an entirely different medium the manganese should be oxidized by bismuthate to the same state of oxidation, other than Mn^{VII}. Since, however, at least two persons in addition to Brinton had observed a discrepancy of the order of 1% between the sodium oxalate and manganese sulfate values, the subject deserved further investigation; not alone from the standpoint of the manganese determination, but also as possibly throwing light upon the composition of permanganate solutions and their action as oxidizing agents. At this point it may be mentioned that the original observations regarding the reduction and reoxidation of the permanganate have been confirmed entirely, with solutions A_1, B, E and G, prepared as shown on p. 1384.

4. *Preparation of Materials and Solutions.* (*a*) *Water.*—Water used in the purification of permanganate and in the preparation of all the permanganate solutions except I and K was distilled three times, the last two being from alkalin permanganate. Water used for the rest of the work was ordinary distilled water of good grade.

(*b*) *Air.*—The air used to deliver the solutions from the stock bottles was washed with acid bichromate solution and alkalin permanganate followed by a column of glass wool.

(*c*) *Asbestos.*—The asbestos used in the filtration of the permanganate solutions and in the bismuthate method was digested for several days with hydrochloric acid, which was finally removed by thorough washing with hot water. It was then suspended in water and the finest portions separated and used in this work. For a few of the experiments this asbestos was ignited, without making, however, any appreciable difference in the results. A two-inch platinum cone, arranged as suggested by Blair,[1] was used for preparing the filter.

(*d*) *Potassium Permanganate.*—Two commercial samples of potassium permanganate were employed, Baker & Adamson's C. P. salt and Kahlbaum's "K" grade. A portion of the former was purified by two recrystallizations in Jena glass flasks, the solutions being electrically heated and filtered through ignited asbestos just before being allowed to crystallize. The fine crystals so obtained were sucked dry on a platinum cone and were then exposed in a thin layer in the dark for four weeks in a vacuum desiccator over concentrated sulfuric acid, the vacuum being maintained at approximately two centimeters. In spite of this long drying, the material was found to contain 0.38% water as determined by heating to decomposition and collecting the water in a weighed calcium chloride tube. When dissolved in pure water and immediately filtered through asbestos, the solution left a slight stain upon the filter. After thorough washing this stain was dissolved with sulphurous acid, and its

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[1] "Chemical Analysis of Iron," 7th ed., p. 123.

manganese content determined colorimetrically, being equal to about 0.01%, *i. e.*, a negligible quantity. Numerous attempts to prepare a permanganate solution which would leave absolutely no stain upon asbestos, proved unsuccessful. Whether such stains were due to the action of the asbestos itself as claimed by Tscheishvili,[1] or to reduction of the permanganate by traces of dust or other reducing substances, could not be determined. The amount of such reduction was, however, negligible, and far less than that observed by Tscheishvili.

(*e*) *Permanganate solutions* were prepared by dissolving a weighed amount of the salt in water; and in the case of the commercial samples, filtering through asbestos to remove manganese peroxide, etc. They were then made up to a definit weight of solution, since the subsequent analyses were conducted entirely with weight burets.

The following solutions were employed in the investigation:

TABLE I.—PERMANGANATE SOLUTIONS USED.

Solution.	Approximate strength.	$KMnO_4$.	H_2O.	Preserved.
A_1	0.03 *N*	Purified	Purified	Dark
A_2	"	"	"	"
B	" + 1% KOH	"	"	"
E	0.1 *N*	"	"	"
G	"	B & A	"	"
I	"	"	Ordinary	Light
K	"	Kahlbaum	"	"

These solutions were preserved in stock bottles provided with an inlet and exit tube with ground glass joint as in an ordinary gas wash bottle. To the inlet tube was sealed a U-tube containing some of the same solution as was in the bottle, thereby preventing changes in concentration of the latter. The exit tube was provided with a three-way stopcock and a tip by which the solution could be delivered to the weight buret by means of purified compressed air.

(*f*) *Stability of Permanganate Solutions.*—At first it was thought necessary to protect these solutions with black paper, but later experiments showed that in the course of several months no appreciable decomposition took place in the solutions exposed to diffused daylight, provided they were first freed from peroxide and were protected from dust and other reducing substances, and that only purified air entered the bottles. Solution I, for example, prepared from ordinary distilled water and permanganate containing appreciable peroxide, which was removed by a single filtration through asbestos, did not suffer decomposition within the limits of observation (one part in two thousand) on standing for two months without protection from the light, even though it was intentionally exposed to bright sunlight for several hours soon after it was prepared.[2]

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[1] *J. Russ. phys. chem. soc.*, **42**, 856 (1910).

[2] Where ordinary distilled water is used, however, it is best to age the solution, or boil it for a short time and then filter out the precipitated manganese dioxide.

In connection with this observation, which simply confirms previous work of others,[1] it is desirable to call attention to another point in connection with the stability of permanganate solutions, which, so far as I know, has not been previously noted, or published. Under conditions which rapidly reduce neutral permanganate solutions, *e. g.*, the presence of dust, reducing gases, or precipitated peroxide, decomposition is greatly retarded by the addition of a small amount of alkali. It was upon the basis of this observation, first noted qualitatively, that solution B was prepared with 1% of potassium hydroxide. Results with this solution were entirely satisfactory, but since the other solutions, when protected from reducing substances, were perfectly stable, the use of alkalin solutions for this work was found unnecessary. Under commercial conditions, however, where it is not always practicable to protect the solutions, the addition of a small amount of alkali will add to their stability.

(*g*) *Manganese Sulfate.*—Pure material was prepared from 300 grams of Kahlbaum's crystallized manganese sulfate ("Zur Analyse"), the operations being conducted entirely in platinum. It was dissolved in water and filtered to remove a small amount of insoluble matter. It was next saturated with hydrogen sulfide, producing a small amount of a black precipitate which was found to contain copper. Additional hydrogen sulfide and a small amount of ammonia produced a precipitate entirely pink, which was filtered out. The hydrogen sulfide was expelled, a few drops of sodium hydroxide were added and the solution was boiled and filtered, the precipitate being found to contain iron. This last operation was twice repeated, the third precipitate being free from iron. An excess of pure, freshly prepared ammonium carbonate was then added and the precipitate of manganese carbonate washed with hot water, by decantation and suction, till free from sulfate. It was dissolved in a slight excess of hydrochloric acid and crystallized twice as $MnCl_2.4H_2O$ (at —5°). The latter crystals were treated with an excess of sulfuric acid and heated in a double-walled platinum dish till almost all the excess sulfuric acid was expelled. The product was entirely soluble in water, and contained a slight excess of sulfuric acid as determined in subsequent tests (Table II A, p. 25).

(*h*) *Sodium Oxalate.*—Two samples were employed, one which had been especially purified by the author for a previous investigation,[2] and a larger sample prepared especially for this Bureau, and which was found to have a reducing value equal to the former, within the limits of one part in two thousand.

(*i*) *Ferrous sulfate* and ferrous ammonium sulfate were employed in-

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[1] Morse, Hopkins and Walker, *Am. Chem. J.*, **18**, 401 (1896); Gardner and North, *J. Soc. Chem. Ind.*, 23, 599 (1904); Warynski and Tscheishvili, *J. chim. phys.*, **6**, 567 (1908).

[2] Blum, THIS JOURNAL, **34**, 123 (1912).

discriminately after it was found that the solutions possessed about the same stability. The C. P. salts as purchased were employed, since their exact composition was not important. For use with 0.03 N permanganate, the solution was prepared according to Blair, with 12.4 g. ferrous ammonium sulfate (or 8.8 g. crystallized ferrous sulfate) and 50 cc. concentrated sulfuric acid per kilogram of solution. For use with 0.1 N permanganate, a solution containing 39.2 g. ferrous ammonium sulfate (or 27.8 g. ferrous sulfate) and 50 cc. concentrated sulfuric acid per kilogram was prepared. If phosphoric acid was employed, as recommended by Dudley,[1] it replaced half of the sulfuric acid in the 0.03 N solutions; but was added in addition to the regular amount of sulfuric acid in the 0.1 N solutions.

Stability of the Ferrous Sulfate Solution.—Incidental observations upon the change in strength of 0.03 N ferrous ammonium sulfate indicated that the rate of oxidation, though slow, was erratic, due no doubt to variations in the extent of its exposure to air. With 0.1 N ferrous sulfate and ferrous ammonium sulfate, the daily rate of oxidation under the conditions used was approximately one part in five hundred, *i. e.*, about 1% in five days, over considerable periods. This rate will depend, no doubt, upon the conditions of its preservation, and is of interest only as indicating how often its strength should be checked up for work of any desired degree of accuracy. Ratios obtained at the beginning and end of various series of determinations showed that no appreciable change took place in a period of a few hours, thus confirming the observation of Baskerville and Stevenson.[2]

(*j*) *Nitric acid* of regular C. P. grade was employed in the concentrated form and diluted to 25% and 3% by volume. The former two solutions were preserved in the dark, since it has been recently shown by Reynolds and Taylor[3] that nitric acid as weak as 10% is decomposed by light, but that recombination takes place in the dark.

(*k*) *Bismuthate.*—Two samples of C. P. sodium bismuthate were employed, one from Baker & Adamson and one from Eimer & Amend. These two samples differed very markedly in appearance, the former being dark brown and the other yellow. In spite of this fact, no difference could be detected between them as regards their suitability for this oxidation. It is well to mention, however, that this compound, of more or less indefinit composition, is somewhat unstable, and if preserved for over six months should be tested for its deficiency of oxidation.

(*l*) *Ferric Nitrate.*—In order to test the effect of ferric salts upon this method, it was necessary to obtain iron, or some salt of iron, which was

[1] Blair, "Chemical Analysis of Iron." 7th ed., p. 125.

[2] THIS JOURNAL, 33, 1104 (1911).

[3] *J. Chem. Soc.*, 101, 131 (1912).

free or practically free from manganese. This proved to be a difficult task, and after testing American ingot iron, and a large number of ferrous and ferric salts, the only one found satisfactory was a sample of Merck's crystallized ferric chloride, which contained less than 0.001% manganese. To convert this to nitrate, it was first converted to sulfate by evaporation to the appearance of fumes with an excess of sulfuric acid, and the sulfate was precipitated with ammonia, washed and dissolved in nitric acid. The resulting salt was free from chloride (of which traces interfere in the bismuthate method) and contained only a small amount of sulfate (which is without effect on this method).

(*m*) *Use of Weight Burets.*—Simple weight burets were made by drawing down the tips of cylindrical graduated separatory funnels (50 and 100 cc.). The increased accuracy gained by the use of weight burets is especially desirable in an operation involving a back titration, and also the ratio of the two solutions used. Weighings were usually made to 0.01 g., except in the case of the smaller amounts of manganese sulfate solutions, which were weighed to 0.005 g. or in some cases 0.001 g. The titrations were usually made in Erlenmeyer flasks of convenient size.

5. *Standardization of Permanganate with Sodium Oxalate.*—Nothing is to be added to the conclusions of McBride,[1] except to emphasize their relation to the present problem. The conditions recommended by him for the standardization of 0.1 *N* permanganate are briefly as follows: Volume of 250 cc., acidity 2% sulfuric acid by volume, initial temperatures, 80°–90°; slow addition of permanganate, especially at beginning and end; final temperature not less than 60°, and end point correction by comparison with a blank containing a known amount of the permanganate. His statement that the variation in results over a wide range of conditions does not exceed one part in a thousand, applies to titrations involving the use of about 50 cc. of 0.1 *N* permanganate. If, however, 0.03 *N* permanganate, commonly used in the bismuthate method, is standardized with sodium oxalate, slight variations in the conditions may cause a relatively much larger error, especially if as is not uncommon, only about 25 cc. of permanganate is employed. For standardization of 0.03 *N* permanganate, the conditions of McBride were employed, except that the initial volume was 75 cc. instead of 250 cc., *i. e.*, the oxalate concentration was about the same as for 0.1 *N* permanganate. In this way the uncertainty in the end point caused by titrating in a large volume with weak permanganate, can be reduced to a minimum. For accurate work, however, the end point correction should be made, since the object of this titration is to determin the absolute oxidizing power of the permanganate. With so small a volume of solution it is usually necessary to reheat it to 60°–70° before completing the titration. These con-

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[1] THIS JOURNAL, 34, 415 (1912).

ditions, as shown by McBride, represent a minimum consumption of permanganate, *i. e.*, the iron or manganese values are a maximum. Any deviation from these conditions will tend to lower the iron or manganese values, which it is believed accounts in part for the discrepancy noted by Brinton and others between values derived from sodium oxalate and from manganese sulfate. For calculation of the manganese value from the sodium oxalate, the factor 0.16397 was employed.

6. *Standardization of Permanganate with Manganous Sulfate.* (*a*) *Standardization of Manganous Sulfate Solutions.*—The two methods commonly used for determining the strength of a manganous sulfate solution are (*a*) precipitation as manganese ammonium phosphate and ignition to pyrophosphate, and (*b*) evaporation of the solution and heating the residue to a certain temperature. Unfortunately both of these will yield high results if the solution contains substances other than manganese sulfate, whether in the original salt or derived from the glass in which the solution is preserved. But even with pure solutions the results are of uncertain accuracy, especially in the case of the pyrophosphate as above mentioned (p. 1380). Weighing as sulfate was therefore adopted as the means of securing a known amount of manganese. The chief source of uncertainty here is the temperature of the final heating, a point upon which the evidence is rather uncertain and contradictory. Volhard[1] was able to obtain constant weight with a special burner, but not with a Bunsen burner. Marignac[2] determined the atomic weight of manganese by heating the sulfate "nearly to red heat." Meineke[3] determined this element as the sulfate, which after being heated to a temperature not stated, was completely soluble in water. Friedheim[4] heated the salt to 360°–400°, while Gooch and Austin[5] obtained constant weight by heating in double crucibles, one centimeter apart, the outer one being at red heat, a procedure since recommended by Treadwell.[6] In determining the water of crystallization of the various hydrates of manganous sulfate, Thorpe and Watts[7] heated the salt to 280°, Linebarger[8] to 170°–180°, and Cottrell[9] to 270°–280°, though the latter found that no decomposition took place at 350°. Richards and Fraprie[10] showed, however, that as much as 0.1% of water remained in the salt after heating for one-half

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[1] *Ann.*, **198**, 318–64 (1879).

[2] *Arch. sci. phys. nat.*, [3] **10**, 25 (1883).

[3] *Chem. Ztg.*, **9**, 1478, 1787 (1885).

[4] *Z. anal. Chem.*, **38**, 687 (1899).

[5] *Am. J. Sci.*, **5**, 209 (1898).

[6] Treadwell-Hall, "Quant. Analysis," II, 104.

[7] *J. Chem. Soc.*, **37**, 113 (1880).

[8] *Am. Chem. J.*, **15**, 225 (1893).

[9] *J. Physic. Chem.*, **4**, 637 (1900).

[10] *Am. Chem. J.*, **26**, 75 (1901).

hour at 350°, but that five minutes heating at 450° produced complete dehydration without decomposition.

Classen[1] and Blair[2] recommend heating to dull red; while Fresenius[3] declares that accurate results can be obtained only by chance, as it is impossible to expel all excess sulfuric acid without decomposing the salt.

The following experiments were conducted to determin the temperature to which manganous sulfate may and must be heated, to expel all the water or excess sulfuric acid and to obtain the normal anhydrous salt. About two grams of the salt were heated in an open platinum crucible in a small electrically heated muffle, temperatures of which up to 400°, were measured with a 450° nitrogen-filled thermometer, and above 400° with a platinum-rhodium thermocouple calibrated at this Bureau. The crucible was kept covered in the desiccator and upon the balance, where it was weighed against a similar crucible as a tare. The results of three series of heatings are shown in Table II, the figures in the last column being calculated from the weight which remained practically constant from 450° to 500°.

TABLE II.—TEMPERATURE OF DECOMPOSITION OF MANGANOUS SULFATE.

A—Manganous sulfate prepared as on p. 1385.

Temp.	Time. hours.	Weight of $MnSO_4$. g.	% of constant weight.	Remarks.
300°	1	2.3655	100.10	
350°	16	49	100.07	
420°	2	42	100.04	
420°	2	40	100.03	
420°	17	37	100.02	
480°	4	33	100.00	
480°	17	32	100.00	
540°	4	31	100.00	
550°	18	29	99.99	
620°	4	25	99.97	Slight darkening

The final product was dissolved in water and the insoluble residue filtered out; washed and ignited, yielding 0.0006 g. Mn_3O_4, equivalent to 0.0004 g. Mn, or 0.0011 g. $MnSO_4$. The filtrate was evaporated for Series B.

B.

Temp.	Time. hours.	Weight of $MnSO_4$. g.	% of constant weight.	Remarks.
300°	3	2.3659	100.15	
340°	18	44	100.10	
400°	4	28	100.03	
440°	18	23	100.00	
480°	5	22	100.00	
480°	18	22	100.00	
570°	5	17	99.98	Slight darkening
570°	18	09	99.95	Decided darkening

A few drops H_2SO_3 + H_2SO_4 were added to the final product, which was then reheated for Series C.

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[1] "Ausgew. Meth. anal. Chem.," I, p. 363.

[2] "Chem. Analysis of Iron," 7th ed., p. 126.

[3] Fresenius-Cohn, "Quant. Analysis," I, p. 297.

TABLE II (*continued*).

Temp.	Time, hours.	Weight of $MnSO_4$, g.	% of constant weight.	Remarks.
			C	
300°	4	2.3717	100.40	
320°	17	690	100.28	
400°	5	41	100.08	
400°	17	34	100.05	
460°	5	23	100.00	
460°	17	23	100.00	
525°	5	21	99.99	
525°	17	19	99.98	
580°	5	17	99.97	Slight darkening
580°	17	08	99.94	Decided darkening

From Table II the following conclusions may be drawn:

1. Manganous sulfate does not undergo any appreciable decomposition upon prolonged heating to temperatures up to 500°.
2. At temperatures from 550°–600° (from incipient to dull redness) this salt decomposes slowly.
3. The anhydrous normal salt can be obtained only by heating, for considerable periods at 450°–500°, especially if an excess of sulfuric acid be originally present.
4. Attempts to obtain the pure salt by heating directly over a flame, or even in a double crucible, without temperature regulation or measurement, must be subject to considerable uncertainty.

Having now a means of obtaining a known weight of manganous sulfate, solutions of known strength (from 0.002 to 0.005 gram manganese per gram of solution) were prepared by dissolving a known weight of the pure salt, heated to constant weight at 450°–500°, and making up to a definit weight of solution, the manganese content of which was calculated by the use of the factor $MnSO_4 \longrightarrow Mn = 0.3638$. In one case, for example, 5.749 grams pure anhydrous $MnSO_4$ was dissolved in water and the solution made up to exactly 1000 grams, producing a solution, one gram of which contained 0.002091 g. Mn, which value was confirmed by evaporation of a weighed portion of the solution and heating to 475° to constant weight. Determinations made by another chemist upon this solution, by evaporation and heating for a short time to "dull redness," yielded the values 0.002100, 2092, 2103, and 2101; the mean value, 0.002099, being therefore 0.38% too high, *i. e.*, an error of about one part in two hundred and fifty. Upon another solution prepared in the above manner, and containing 0.002000 g. Mn per gram solution the same chemist obtained by direct heating to dull redness 0.002004, 2006 and 2005, *i. e.*, the results were high, in spite of the fact that in the latter series at least, very slight decomposition had evidently taken place in the bottom of the crucible. Apparently, therefore, those parts of the salt on the sides of the crucible had not been heated to the necessary temperature for a sufficient length of time to expel all water or excess of acid. In view of these facts, the desirability of substituting for the manganous sulfate some other standard, such as sodium oxalate, is very evident.

(*b*) *Effect of Conditions upon Standardization with Manganous Sulfate.*

(1) *Ferrous Sulfate-Permanganate Ratio.*—This ratio, which is fundamental for the accuracy of the method, is usually determined by means of a blank experiment, that is, a determination is run through in the absence of manganese, under the conditions to be used in the regular analysis. This procedure, which was evidently devised for the purpose of eliminating errors due to impurities in the reagents, has been found to be unnecessary, *i. e.*, the ratio so obtained is the same as that obtained by direct titration of the ferrous sulfate in the same volume. This is due to the fact that on the one hand the bismuthate oxidizes readily any traces of nitrous acid which may be present in the nitric acid; and that on the other hand nitric acid of the strength present in the final solution, does not have any effect upon the ferrous salt in the short time necessary for a titration. If, however, the ferrous salt be titrated in the presence of nitric acid containing small amounts of nitrous acid, which has not been treated with bismuthate, an excessive amount of permanganate will be consumed, due to the reducing action of the nitrous acid upon the permanganate, which takes place more readily in the presence of ferrous salt than in its absence. It must be clearly understood that conducting the blank experiment in the usual way does not obviate the necessity of avoiding the presence of nitrous acid in the solutions of manganese used in the standardizations or analyses, since, as indicated by Blair,[1] nitrous acid will reduce part of the permanganic acid, precipitating manganese peroxide, which is not reoxidized by the bismuthate.

While not strictly necessary, the determination of this ratio by means of a blank, affords a convenient means of testing the efficacy of the filter, and has therefore been followed in all this work. The conditions found most satisfactory are as follows: To 50 cc. of nitric acid (25% by volume), add a small amount of bismuthate. Shake and allow to stand a few minutes, dilute with 50 cc. of 3% nitric acid, filter through the asbestos filter and wash with 100 cc. of 3% nitric acid. To the filtrate, which should be perfectly clear, add a volume of ferrous sulfate approximately equal to that to be used in the subsequent determinations (25 to 50 cc.) and titrate at once to the first visible pink. Even for the most accurate work, no end point correction is required for this titration, provided only that the solutions are always titrated to the same color, and that about the same volumes are used in the standardization and analyses.

(2) *Amount of Manganese Present in a Determination.*—One of the

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[1] 7th ed., p. 128.

serious limitations of this method is the small amount of manganese generally determined, making it somewhat unreliable for high grade materials. Blair recommends the presence of from 0.01 to 0.02 g. Mn, involving the use of a sample of manganese ore of only 0.02 g. obtained by taking an aliquot of the solution of a gram of the ore. Ibbotson and Brearley[1] state that the method is equally applicable for large or small amounts of manganese without, however, giving the evidence for this conclusion. Since with 0.03 *N* permanganate, 0.015 g. Mn is the largest amount that can be conveniently determined, the following experiments were conducted with approximately 0.1 *N* $KMnO_4$ and $FeSO_4$. The results are expressed in terms of the manganese value of one gram of the permanganate solution. It should be noted that a high result indicates incomplete oxidation of the manganese by the bismuthate. In these and

TABLE III.—EFFECT OF AMOUNT OF MANGANESE IN THE PRESENCE OF VARIABLE AMOUNTS OF IRON.

$KMnO_4$ Solution I.

Manganese values calculated from			
Sodium oxalate. Values determined over a period of three weeks.	Manganous sulfate.		
	Gram manganese present.	Gram iron present.	1 g. $KMnO_4$ solution = g. Mn.
	A.		
0.001090	0.03	...	0.001088
91	"	...	88
92	"	1.0	89
92	"	"	89
91	"	"	91
91	"	"	92
	B.		
91	0.05	...	90
92	"	...	92
91	"	...	90
92	"	...	87
90	"	...	90
90	"	1.0	89
89	"	2.0	90
92	"	3.0	89
	C.		
91	0.10	...	89
91	"	...	89
90	"	...	1161
90	"	...	1089
	"	...	97
	"	...	96
	"	...	1107
	"	...	1088
Av. 0.001091		Av. of A and B	0.001089

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[1] *Chem. News*, 82, 269 (1900).

the following series the following conditions were tentatively employed, and the variation produced by a change of one condition was noted in each series of experiments. The manganese sulfate was oxidized at room temperature in a volume of about 50 cc., containing 25% nitric acid by volume. An excess of bismuthate (about 0.5 g.) was added, the solution was agitated for one minute, the sides of the flask were rinsed down with 50 cc. of 3% nitric acid, and the solution at once filtered with suction through the asbestos filter, previously coated with bismuthate. The flask and filter were washed several times with 3% nitric acid of which about 100 cc. was used. The filtration and washing required from 1 to 3 minutes. To the filtrate ferrous sulfate was added immediately in slight excess, which was at once titrated with permanganate.

From Table III it is evident that for amounts of manganese up to 0.05 g. the method is accurate within the limits of error, *i. e.*, about one part in five hundred, while results obtained with as much as 0.10 g. Mn are decidedly erratic, only one-half approaching the correct values. It is apparent, therefore, that about 0.05 g. Mn is the practical limit under these conditions. This amount is, however, far more satisfactory than only 0.01–0.02 g., and permits the use of 0.10 g. of high grade manganese ore, a decided advantage. As seen in series A and B, the results with as much as 3 g. iron present, are entirely satisfactory. The agreement of the sodium oxalate and manganese sulfate values will be discussed later.

(3) *Acidity, Volume, Time of Standing, Etc.*—The results of several series of experiments to determin the effect of various conditions upon the bismuthate method are summarized in the following table:

TABLE IV.—EFFECT OF CONDITIONS UPON BISMUTHATE STANDARDIZATION.
$KMnO_4$ Solution K.

Series.	Method.	Modification.	No. of detns.	1 g. $KMnO_4$ solution = g. Mn.
A 1	$Na_2C_2O_4$	Standard—p	6	0.001098
B 1	$MnSO_4$	Standard—p	9	1098
C 1	"	Initial conc. HNO_3—10%	3	1114
2	"	Initial conc. HNO_3—40%	3	1098
D 1	"	Initial volume—150 cc.	3	1098
E 1	"	Shaken with bismuthate—15 sec.	3	1097
F 1	"	Stood before filtration 10 min.	3	1097
2	"	Stood before filtration 30 min.	1	1097
G 1	"	Stood after filtration 10 min.	1	1097
2	"	Stood after filtration 20 min.	1	1097
3	"	Stood after filtration 30 min.	1	1098
H 1	"	Stood after addition of $FeSO_4$—10 min.	1	1096
2	"	Stood after addition of $FeSO_4$—30 min.	1	1084
I 1	"	Addition of H_3PO_4—5 cc.	3	1099
		Mean of all $MnSO_4$ values except C_1 and H_2,		0.001098

Of the $MnSO_4$ values given in Table IV, the individual determinations of all except those in C_1 and H_2, varied less than one part in five hundred from the mean, showing that accurate results can be obtained over a very wide range of conditions. The only conditions found to produce appreciable errors were (*a*) deficiency of nitric acid, and (*b*) allowing the solution to stand more than ten minutes after the addition of the ferrous sulfate, of which about 10 cc. excess was present. Since there is no occasion for either of these conditions to arise in good practice, the method may be considered accurate under all ordinary conditions of procedure, an important criterion for a standard method of analysis.

Use of Phosphoric Acid.—The addition of this reagent as recommended by Dudley, was found convenient, though not necessary, since with 0.1 *N* solutions there was no difficulty in obtaining a sharp end point within 0.03 cc. of permanganate, without its use. If used, it should be added to the ferrous sulfate solution beforehand, rather than during the titration, since in the latter case a white precipitate, probably consisting of basic bismuth phosphate separates, rendering the end point slightly less distinct. With very large amounts of iron, *e. g.*, 3–5 g., such as would have to be used if manganese in steel were determined with 0.1 *N* permanganate, it was found that addition of phosphoric acid possesses no advantage, since it tends to produce a pink color, due probably to the formation of an acid ferric phosphate,[1] which obscures the end point as much as does the ferric nitrate. The use of 0.1 *N* solutions is therefore recommended only for manganese ores and similar high grade products, in which the highest accuracy is desired.

(*c*) *Probable Course of Reactions.*—From Table IV some light may be thrown upon the probable course of the reactions when manganese is oxidized by bismuthate. At least two reactions are probable, (*a*) direct oxidation to Mn^{VII}, and (*b*) interaction of unoxidized Mn^{II} with the Mn^{VII}, precipitating Mn^{IV}, which is then removed from the oxidizing influence of the bismuthate. If these two reactions may take place, the problem resolves itself into a determination of the conditions under which reaction (*a*) will be accelerated and (*b*) will be retarded, so that (*a*) goes practically to completion before (*b*) can take place to an appreciable extent. The favorable conditions for (*b*) as conducted in the Volhard method for example, are slight acidity and high temperature, which should therefore be avoided in the bismuthate oxidation. That this explanation is plausible is shown by a comparison of C_1 and C_2. That complete oxidation may be effected in a short time is indicated in E_1, in which connection the necessity for thorough agitation must be emphasized. Other experiments, not recorded here, showed that with 0.05 g. or more of Mn, complete oxidation could not be effected if the solution

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[1] Erlenmeyer and Heinrich, *Ann.*, 190, 191 (1877).

was not thoroughly agitated. In the earlier experiments in this investigation, the solutions were artificially cooled to about 5°; but after it was found that results at room temperature, 20°–25°, were entirely satisfactory, artificial cooling was dispensed with.

(*d*) *Conditions Recommended.*—Correct results can be obtained under the following conditions: To the manganese solution containing 20–40% nitric acid (free from nitrous acid) in a volume of 50–150 cc., add a slight excess of bismuthate (usually 0.5 to 1.0 gram), agitate thoroughly for about one-half minute, wash down the sides of the flask with 3% nitric acid, filter through asbestos, add a slight excess of ferrous sulfate, and titrate at once with permanganate. For iron and steel, 0.03 *N* solutions as described by Blair are satisfactory.

For ores and ferromanganese 0.1 *N* permanganate solution may be employed, and an amount of material containing about 0.05 gram manganese. For the rapid solution of ores, a method recommended by Blair[1] has been found convenient. One gram of the ore is fused in a large platinum crucible with 10 grams potassium bisulfate, one gram of sodium sulfite and 0.5 gram sodium fluoride. The heating should be very slow till effervescence ceases. After complete fusion the product is cooled, then heated carefully with 10 cc. concentrated sulfuric acid, cooled, dissolved in water, and made up to a definit volume. The slight precipitate of barium sulfate usually present will not influence the manganese determination.

7. *Agreement of Values Derived from Sodium Oxalate and Manganous Sulfate.*—Consideration of the values in Table V shows plainly that no greater difference than one part in five hundred exists between the results derived from sodium oxalate and manganese sulfate, respectively, instead of the former values being one per cent lower, as claimed by Brinton and others. In fact, in the case of the 0.1 *N* solutions, the only ones in which the accuracy of more than one part in five hundred is realizable, the manganous sulfate values show a tendency to be from one to two parts per thousand lower than the sodium oxalate results. It is at least interesting, though

TABLE V.—COMPARISON OF $Na_2C_2O_4$ AND $MnSO_4$ VALUES.

	Manganese values derived from			
	Sodium oxalate.		Manganese sulfate.	
Permanganate solution.	No. of detns.	1 g. $KMnO_4$ soln. = g. Mn.	No. of detns.	1 g. $KMnO_4$ soln. = g. Mn.
A_1	3	0.0003465	3	0.0003469
A_2	4	0.0003462	3	0.0003462
B	6	0.0003454	5	0.0003458
E	9	0.001096	4	0.001094
G	7	0.001091	5	0.001090
I	18	0.001091	28	0.001089
K	6	0.001098	29	0.001098

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[1] Private communication.

perhaps not significant, that if the value 55.00 instead of 54.93 be used for the atomic weight of manganese, the results with the 0.1 *N* solutions agree in every case to within one part in a thousand.

8. *Analysis of Pure Permanganate Crystals.*—Additional evidence of the correctness of the above values was found in the analysis of the pure permanganate, prepared as described on p. 1383, which contained 0.38% water. The salt should therefore contain 34.63% manganese, instead of 34.76%, the theoretical content for pure anhydrous $KMnO_4$. This difference with specially purified permanganate indicates clearly the probable presence of water as well as manganese peroxide in C. P. permanganate, rendering it unsuitable as a primary standard. Manganese was determined gravimetrically by precipitation with ammonium sulfide; the manganese sulfide being washed with dilute ammonium sulfide, ignited in a weighed crucible, treated with sulfurous and sulfuric acids, evaporated, heated to 450° to constant weight, and weighed as $MnSO_4$. The manganese in the filtrates was determined colorimetrically. Results of duplicate analyses were 34.70% and 34.66%, the mean 34.68% agreeing closely with the theoretical value 34.63%. The oxidizing value of this permanganate was determined by means of solutions A_1, A_2, and E (Table V) which were prepared by the solution of an exact weight of the salt in a definit weight of solution. In A_1 and A_2, exactly one gram $KMnO_4$ was dissolved and diluted to one kilogram, yielding solutions having an oxidizing value equivalent to 34.65% Mn (average of all sodium oxalate and manganous sulfate values for A_1 and A_2). Solution E contained 3.1606 g. of the salt per kilogram, and possessed an oxidizing power equivalent to 34.65% Mn (derived from the average of all sodium oxalate and manganous sulfate values for solution E). Solutions B, G, I and K were prepared of only approximately the desired strength, and the results have no relation to the composition of the solid permanganate employed.

9. *Analysis of Manganese Ores.*—Analyses of the Bureau of Standards manganese ore (Standard sample No. 25) by means of permanganate I, gave as the average of nine determinations, 56.30% Mn upon the basis of the sodium oxalate standardization, and 56.20% if calculated from the manganous sulfate. These results are in good agreement with the mean value 56.36% derived from all determinations upon the certificate, and with the value 56.33 formerly found by the author with the bismuthate method, using sodium oxalate as the standard. Unfortunately, comparisons based upon this sample are not necessarily conclusive, since the mean value 56.36% is derived from results ranging from 56.15 to 56.63, obtained by eight chemists using a variety of methods, the lack of agreement of which is illustrated. If the bismuthate results by the author are correct, a conclusion made highly probable by the work here described, the value of the ore lies between 56.20 and 56.30% manganese, and many

of the values found by other methods, by the author and others, are too high. That the tendency of many commercial methods is to yield results higher than those by the method here recommended, is shown in the results of analyses of three manganese ores by the author and two well known commercial chemists.

TABLE VI.—ANALYSES OF MANGANESE ORES.

Analyst.	Method.	Ore I.	Ore II.	Ore III.
A	Bismuthate	52.47	52.53	50.50
B	Modified acetate	52.40	52.29	50.52
Author	Bismuthate	51.93	52.03	50.12

The differences here shown, amounting to 0.8 to 1.0% of the manganese present, are by no means insignificant. The discrepancy between the results by A and the author, both using the bismuthate method, was found to be due mainly to differences in the method of standardizing the manganous sulfate solution (see p. 1388). These results show clearly the necessity for a thorough investigation of other methods for determining manganese, in order that accurate results may be uniformly obtained.

III. Summary.

1. To obtain normal, anhydrous manganous sulfate, the salt may and must be heated for a considerable time at 450°-500°.

2. Standardizations of permanganate solutions (both 0.03 *N* and 0.1 *N*) by means of sodium oxalate, manganous sulfate and solid permanganate agree within the experimental error, which in the bismuthate method could not be reduced much below one part in five hundred. Taken together with the agreement of sodium oxalate and iron values, and the experiments upon the reduction and reoxidation of permanganate, the absolute accuracy of the above results, within the experimental limits, is rendered almost certain.

3. In view of the difficulties attending the use of manganous sulfate, standardization by means of sodium oxalate, under definit, but easily realizable conditions, is recommended.

4. Results by the bismuthate method are accurate over a very wide range of conditions, for amounts of manganese up to 0.05 gram.

5. For accurate determinations on rich ores, etc., the use of 0.1 *N* permanganate is recommended, while for iron and steel the method described by Blair is entirely satisfactory.

6. The statement of Blair that "this method for materials containing small amounts of manganese, say up to 2%, is more accurate than any other method, volumetric or gravimetric," may be extended to include materials containing large amounts of manganese.

7. Filtered permanganate solutions preserve their strength when exposed to diffused light, if protected from dust and reducing substances.

In the presence of the latter, alkalin permanganate solutions decompose less rapidly than do neutral solutions.

The author desires to express his thanks to Dr. W. F. Hillebrand for valuable suggestions and advice during the course of this investigation.

NOTE.

"*A Safety Siphon.*"—In many laboratories, a need is felt for some efficient means of handling solutions. When poured out of a bottle, they are often spilled, and besides being dangerous to clothing, give the laboratory an untidy appearance. Other solutions, of which small quantities are used at a time, are wasted and spoiled by being transferred to individual burets.

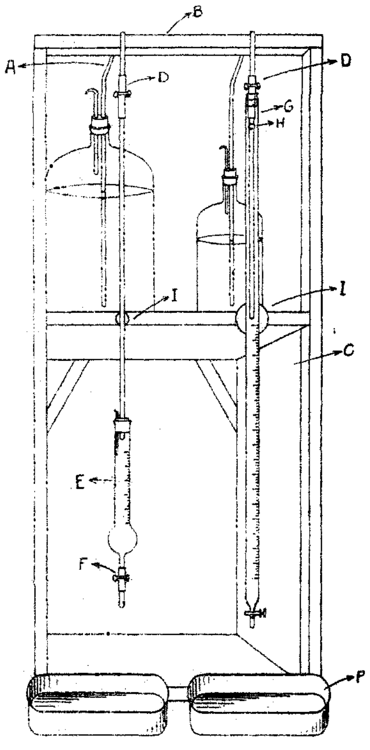

Fig. I.

The apparatus shown was devised for distributing solutions to the students in the food laboratory.

Fig. 1. An ordinary siphon "A" was constructed, the tube being supported by the rack "B" attached to the box "C" on which the bottles were placed. Rubber connections with pinch-cocks were placed at D, well above the liquid in the bottle. In case an accident happens to the connection, the liquid will not siphon out as it would if the joint were lower down. To the lower end of the siphon tube, a graduated cylinder "E" was placed, it being made from a large calcium chloride tube, or Kjeldahl receiving tube and graduated as desired. To the bottom is attached a rubber connection with pinch-cock.

In order to obtain any of the liquid, the desired amount is first drawn out of the bottle by opening "D." After this pinch-cock is closed, the liquid can be drawn out of the graduated tube by opening "F." Having two pinch-cocks, the danger of leaving the stopcock "D" open is avoided and waste is done away with.

The other siphon is fitted up with an ordinary buret, slipped up over the siphon tube and held at "G" by a rubber connection. A small hole blown at "H," allows air to enter when the liquid is drawn off below. Readings are taken below the inner tube.