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

THE VOLUMETRIC DETERMINATION OF HYDROXYLAMINE.

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In the present investigation 3 volumetric methods of determining hydroxylamine in aqueous solution have been studied:

The titanous salt method,[1] in which the hydroxylamine is reduced by excess titanous salt in acid solution with exclusion of air, and the excess titrated with permanganate.

$$2NH_2OH + Ti_2(SO_4)_3 = (NH_4)_2SO_4 + 4TiOSO_4 + H_2SO_4. \quad (1)$$

The ferric salt method,[2] in which the hydroxylamine is oxidized in an acid solution by excess of a ferric salt, the mixture is boiled and the ferrous salt formed titrated with permanganate.

$$2NH_2OH + 2Fe_2(SO_4)_3 = N_2O + 4FeSO_4 + 2H_2SO_4 + H_2O. \quad (2)$$

The iodine method,[3] in which the hydroxylamine is oxidized by iodine in a neutral solution, *e. g.*, in the presence of disodium phosphate.

$$2NH_2OH + 2I_2 = N_2O + 4HI + H_2O \quad (3)$$

or

$$2NH_2OH + 2I_3^- = N_2O + 6I^- + 4H^+ + H_2O.$$

Our first experiments, with the iodine method, yielded irregular results which could not be interpreted until the concentration of the hydroxylamine solution was accurately determined. An examination of the literature showed a rather unsatisfactory state of affairs. The advocates of the ferric sulfate method furnish evidence that it is perfectly reliable, but Leuba[4] gives detailed experimental data to prove the contrary, and Adams[5] states that he could not obtain reproducible results with it. The investigators who have used the iodine method consider it to be fairly satisfactory, but some of them state that it is not very accurate, and Rupp and Maeder[6] have recently concluded that correct results are obtained only by a compensation of errors. Accordingly a study of various methods of standardizing an hydroxylamine salt solution was undertaken.

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[1] A. Staehler, *Ber.*, **37**, 4732 (1904); 42, 2695 (1909).

[2] W. Meyeringh, *Ibid.*, **10**, 1942 (1877); F. Raschig, *Ann.*, 241, 191 (1887); *Z. angew. Chem.*, **17**, 1411 (1904); Ebler and Schott, *J. prakt. Chem.*, [2] **78**, 320 (1908); Rupp and Maeder, *Arch. Pharm.*, 251, 297 (1913); Sommer and Templin, *Ber.*, **47**, 1226 (1914).

[3] W. Meyeringh, *Ber.*, 10, 1940 (1877); T. Haga, *J. Chem. Soc.*, **51**, 794 (1887); M. Adams, *Am. Chem. J.*, **28**, 198 (1902); A. W. Stewart, *J. Chem. Soc.*, **87**, 410 (1905); Petrenko-Kritschenko and Kantacheff, *Ber.*, **39**, 1453 (1906); Acree and Johnson, *Am. Chem. J.*, **38**, 316 (1907); Barrett and Lapworth, *J. Chem. Soc.*, **93**, 85 (1908).

[4] Leuba, *Ann. chim. anal. appl.*, **9**, 246 (1904)

[5] Adams, *Am. Chem. J.*, **28**, 198 (1902).

[6] Rupp and Maeder, *Arch. Pharm.*, **251**, 295 (1913).

The ferric salt and titanous salt methods were proved to be perfectly concordant.[1] Since the one method depends upon the oxidation of hydroxylamine to nitrous oxide and the other upon its reduction to NH_4^+ it follows that both methods must be accurate. The task of comparison was simplified by the fact that the results of both methods of analysis were obtained for the same solution of hydroxylamine sulfate and were referred to the same permanganate solution; possible errors in the calibration of pipets and burets and in the standardization of the reference solution were thus eliminated.

The Titanous Salt Method.

The use of an acid solution of a titanous salt as a standard reducing agent[2] deserves more attention than it appears to have received. The necessary precaution of excluding the oxygen of the air from the stock solution and during titrations is easily taken by means of carbon dioxide gas, and the preparation of the stock solution by reducing a titanium salt solution is not a very difficult task.

A solution of titanium sulfate, approximately 0.1 molar, and containing 5% of sulfuric acid, was prepared by dissolving titanium dioxide in conc. sulfuric acid and diluting to the proper volume. This was reduced by the method of Van Brunt[3] in a 20-inch Jones reductor heated electrically by a resistance coil which surrounded the lower part of the reductor tube. The reductor was half filled with amalgamated granular zinc which was kept covered with 5% sulfuric acid when not in use. Reduction was rapid at a temperature below the boiling point, and the purplish black color showed the progess of the reduction. The wide upper end of the reductor was closed with a rubber stopper fitted with a dropping funnel to hold the solution, and with a vent which could be closed to force the reduced solution into the container. Through the latter a current of carbon dioxide was passed.

A 75 to 100 cc. portion of titanium sulfate solution was reduced in each operation. Time was saved by warming the solution before introducing it into the reductor, and 15 to 20 minutes was then sufficient for each treatment. With a little practice, a liter of solution can be reduced in 4 hours. One difficulty must be noted: the solution should not be boiled either before or during reduction, since a precipitate may then form. On this account no attempt was made to completely reduce the titanium in the solution.

The titanous sulfate solution (approximately 0.1 *N*) was shaken and

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[1] This result is in agreement with Staehler's conclusion from two analyses, one by each method, which differed by only 0.5%; A. Staehler, *Ber.*, **37**, 4732 (1904).

[2] Treadwell-Hall, *Quant. Anal.*, 1912, pp. 699–701; Knechtand Hibbert, *Ber.*, 36, 1549 (1903); 38, 3318 (1905).

[3] Van Brunt, THIS JOURNAL, 36, 1426 (1914).

allowed to stand several hours before being used. The solution when needed was siphoned into a buret filled with carbon dioxide; the tip of the buret was inserted through a rubber stopper into an Erlenmeyer titration flask; carbon dioxide was passed into the flask and escaped through the hole in the cork into which the buret tip was inserted. The container and the top of the buret were permanently connected with the carbon dioxide supply.

The concentration of the solution was determined, just before use with hydroxylamine, by means of 0.1 *N* potassium permanganate solution, which had been standardized against Bureau of Standards sodium oxalate. In each titration 20 to 25 cc. solution was run into the titration flask, the buret tip was slipped out of the hole in the rubber stopper, the tip of the permanganate buret inserted, and the potassium permanganate added at once to a faint pink.

The hydroxylamine solution was analyzed as follows: 10 cc. approximately 0.2 *N*, or 20 cc. 0.1 *N*, hydroxylamine was placed in the titration flask; about twice the theoretical amount of titanous sulfate was added from the buret; after 8 to 10 minutes the excess was titrated with the permanganate solution.

Two titanous sulfate solutions were prepared. Each was standardized on the day the corresponding hydroxylamine results given below were obtained:

First solution, 0.09887 *N*, 0.09893 *N*. Average, 0.0989 *N*.
Second solution, 0.1056 *N*, 0.1058 *N*, 0.1057 *N*. Average, 0.1057 *N*.

It follows that the titanous sulfate-permanganate titration is reproducible to 0.1 or 0.2%.

Four consecutive hydroxylamine determinations, made with the aid of the first titanous sulfate solution, yielded the following results:

10.00 cc. of NH_2OH solution is equivalent to 18.62, 18.69, 18.69, 18.61 cc. of 0.1 *N* $KMnO_4$.
Concentration of NH_2OH, calculated from average, 0.1864 *N*.
Concentration of NH_2OH, by ferric sulfate method, see below, 0.1865 *N*.

Another set of results with a different hydroxylamine sulfate solution was obtained with the second titanous sulfate solution.

20.00 cc. of NH_2OH solution is equivalent to 21.48, 21.62, 21.62, 21.77 cc. of 0.1 *N* $KMnO_4$.
Concentration of NH_2OH, calculated from average, 0.1081 *N*.
Concentration of NH_2OH, by ferric sulfate method, see below, 0.1081 *N*.

The individual determinations of hydroxylamine by the titanium method agree within a few tenths of per cent., and therefore, as will be seen later, this method is as satisfactory as the ferric sulfate method. The agreement of the average values from the two methods is better than was to be expected, and furnishes a definite proof of the correctness of both methods.

The Ferric Salt Method.

Dilute solutions of hydroxylamine sulfate were analyzed as follows: 10 cc. of approximately 0.2 *N* hydroxylamine (or 20 or 25 cc. of approximately 0.1 *N* strength) were pipetted into a 400 cc. Erlenmeyer flask which contained 50 cc. of ferric sulfate solution (40 g. of $Fe_2(SO_4)_3.9H_2O$ per liter) and 15 cc. of sulfuric acid (approximately 12 *N*); the mixture was boiled vigorously for 5 minutes, cooled, made up to about 200 cc. with water and titrated with 0.1 *N* permanganate solution.

The results obtained with one solution follow:

10.00 cc. of solution, 18.84, 18.39, 18.43, 18.61, 18.61 cc. of 0.1 *N* $KMnO_4$ (concentration, from average, 0.1860 *N* NH_2OH).

After 3 weeks, 18.59, 18.69, 18.64 cc. (average, 0.1864 *N* NH_2OH).

After 6 weeks, 18.63, 18.69, 18.64 cc. (average, 0.1865 *N* NH_2OH).

Equally satisfactory results were obtained with other solutions. It is evident that the results are reproducible to within a few tenths of a per cent. and that the hydroxylamine sulfate solution undergoes little, if any, change of concentration over a considerable period of time.

In the above experiments the hydroxylamine solution was added to the ferric sulfate-sulfuric acid solution at room temperature, and a few minutes elapsed before the solution could be heated to boiling. The following data show that the result is not appreciably altered when the hydroxylamine is added to a boiling solution:

20.00 cc. of NH_2OH solution, usual method, 21.62, 21.65, 21.62, 21.60 cc. of 0.1 *N* $KMnO_4$ (concentration, from average, 0.1081 *N* NH_2OH).

20.00 cc. of NH_2OH solution, added to a boiling $Fe_2(SO_4)_3$ solution, 21.72, 21.66 cc.

The time of vigorous boiling may be made longer than 5 minutes. One experiment in which this time was 20 minutes agreed with the reference experiments within 0.4%.

The already large excess of ferric salt (about 3-fold) may be greatly increased. In one experiment in which 3 times the usual volume of ferric sulfate solution was added the result was unchanged.

The presence of ammonium salts in large amount does not affect the results, and the ferric sulfate can be replaced by ammonium iron alum. One of several series of results with 10.00 cc. of hydroxylamine sulfate solution, 40 cc. of a solution of ammonium iron alum saturated at room temperature, and sulfuric acid is given.

18.67, 18.67, 18.67, 18.68 cc. of 0.1 *N* $KMnO_4$.

The average of a series with ferric sulfate instead of the iron alum (18.62 cc.) agreed with these results within 0.3%.

The conditions outlined above for the analysis are those originally recommended by Raschig, *viz.*, the large excess of ferric salt, the boiling, and the presence of acid. Our results thus confirm the work of those who endorsed the method, and disprove the criticisms of Adams. Of the detailed results of Leuba only one was obtained under the conditions recommended, and this discordant result must be rejected.

That errors will result when the analysis is made under other conditions was pointed out by Raschig. He emphasized especially the large error that will be made if the permanganate is added before the reaction (Equation 2) is completed: too much potassium permanganate is then used, and nitrogen is oxidized beyond the nitrous oxide stage. Leuba's results (except the one referred to in the preceding paragraph) illustrate the magnitude of this error, *e. g.*, 55% and 30% excess permanganate was required after the hydroxylamine, excess ferric alum, and sulfuric acid had been digested for $^3/_4$ hour at 26° and 82°, respectively.

If the permanganate is added while hydroxylamine is still present an error of this kind will result. Raschig[1] investigated this reaction in the presence of sulfuric acid (and absence of ferric sulfate); the amount of permanganate varied from about 2 to 1.5 times that necessary to form nitrous oxide, while the temperature of the hydroxylamine solution was varied between room temperature and 100°. Raschig accordingly rejected the permanganate method of analysis.[2]

With regard to the reaction between hydroxylamine and excess ferric sulfate Raschig[3] concluded that the hydroxylamine was rapidly used up, and that the positive error was due mainly to the presence of an intermediate substance, nitroxyl, NOH,—which was completely transformed into nitrous oxide by the 5-minute boiling. The recent work of Angeli[4] furnishes additional evidence in favor of nitroxyl as a possible intermediate step; but the existing evidence is scarcely sufficient to enable us to determine just when the positive error is due to reaction of potassium permanganate with hydroxylamine and when due to nitroxyl. That it is not due to a reaction between potassium permanganate and nitrous oxide we found by a direct experiment.

While the necessity of boiling the solution had thus been demonstrated, we did not find quantitative data with regard to the errors that might result from a variation of the concentrations of acid and ferric sulfate. To obtain this information the following experiments were performed in this laboratory by Dr. H. E. Miller.

Effect of Varying Concentration of Acid.—The experiments listed below followed the standard precedure: the volume noted in the fifth volumn is the volume of solution boiled for 5 minutes. Dilution to 200 cc. after cooling was found to have no effect on the amount of permanganate used in the titration.

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[1] Raschig, *Ann.*, **241**, 188 (1887).

[2] In spite of this warning the method has been used. Cf. Patten and McCaughey, *Trans. Am. Electrochem. Soc.*, **15**, 544 (1909).

[3] Raschig, *Z. angew. Chem.*, **17**, 1411 (1904).

[4] Angeli, *Ahrens' Sammlung*, **13**, 1 (1908).

No.	Cc ferric sulfate.	Cc. 12 N H_2SO_4.	Volume. Cc.	Cc. $KMnO_4$.			Titration result, % theoretical.
Using 25 cc. of Hydroxylamine Solution.							
1	50	15	90	23.0,	23.05,	23.0	100%
2	50	15	101	23.0,	22.95,	...	100%
3	50	7.5	86	22.95,	23.0	22.90	99.8%
4	25	4	101	22.90,	...	...	99.6%
5	50	2	75	22.74	...	...	98.9%
6	25	1	75	22.60,	22.65	...	98.4%
7	50	0	100	22.23	...	...	96.6%
8	50	NaAc	100	22.20	...	...	96.5%
Using 10 cc. of Hydroxylamine Solution.							
9	25	0	75	8.85	...	...	96.2%
10	25	NaAc	75	8.85,	8.92	...	96.6%

These results show that a lowering of the concentration of the sulfuric acid produces a negative error. The error is negligible when the amount of acid used is half that recommended in the standard procedure, but may be as large as 3 or 4% when no acid is used. Expts. 8 and 10 were duplicates of 7 and 9, respectively, except that sodium acetate was added initially to the ferric sulfate solution in order to keep the hydrogen ion concentration low during the reaction. However, although the acid formed in the reaction made the hydrogen ion concentration higher in Expts. 7 and 9, the results were practically the same as in Expts. 8 and 10.

After some experimentation this negative error was found to be due to the oxidation of ferrous salt by oxygen of the air. This reaction occurs mainly during the first stage of the operation while the solution is being heated from room temperature to the boiling point. In an acid solution at room temperature in 1 hour there is no appreciable oxidation of ferrous sulfate solution in contact with air.

Some of the above experiments were repeated in an atmosphere of carbon dioxide (which contained only about 0.1% oxygen); the ferric sulfate solution was boiled to expel the air and cooled under carbon dioxide, the hydroxylamine was added, the mixture was boiled for 5 minutes, some sulfuric acid was added, the mixture was again boiled, and cooled under carbon dioxide. The apparatus consisted of an Erlenmeyer flask closed with a 3-hole rubber stopper, fitted with an inlet and outlet for carbon dioxide and a separating funnel (with stopcock) for introducing the hydroxylamine. The experiments are numbered to show the relation to the corresponding experiments in the first table.

Experiments in an atmosphere of carbon dioxide.

3(*b*), Vol. = 100 cc.: 23.02, 23.0, 22.95 cc. $KMnO_4$ (100% instead of 99.8%).
5(*b*), Vol. = 100 cc.: 22.92 (99.7% instead of 99.6%).
7(*b*), Vol. = 100 cc.: 22.65, 22.64, 22.68, 22.82 (98.6–99.2% instead of 96.6%).

In these experiments the error was greatly reduced; and, since the elimination of air could scarcely have been complete, it seemed probable that the negative error was due solely to the oxygen in the air.

Finally we tried the elimination of this error by the simple method of boiling the ferrous sulfate solution to expel the air, and introducing the hydroxylamine into the boiling solution from a pipet. Otherwise the experimental conditions were the same as in Expt. 7.

No. 7(*c*), Vol. = 75 cc.: 23.0, 23.0 cc. $KMnO_4$, 100%.

There are therefore two satisfactory methods of preventing an error due to the oxidation of the ferrous salt by oxygen of the air:

(1) by the use of the regular procedure; the hydroxylamine is added at room temperature to excess ferric sulfate in a solution which is 2 to 3 normal with respect to sulfuric acid;

(2) by adding the hydroxylamine slowly to a boiling ferric sulfate solution.

Effect of Varying Ferric Sulfate Excess.—The experiments listed below were performed by the regular procedure. The ferric sulfate was much less than the usual amount, except in Expts. 11, 12 and 13. The amount is shown in the third column as number of equivalents in terms of the hydroxylamine used. Thus 1.40 means that the amount of ferric sulfate was 40% greater than the theoretical amount necessary to oxidize hydroxylamine to nitrous oxide; 25 cc. of ferric sulfate was in theory sufficient to oxidize 38.4 cc. hydroxylamine solution. It is to be noted that in Expts. 21–25 the amount of acid was much less than usual.

No.	Ferric sulfate referred to NH_2OH.	Cc. 12 *N* H_2SO_4.	Volume. Cc.	Cc. $KMnO_4$.	Titration result, % theoretical.
Using 25 cc. of Hydroxylamine Solution.					
11	2.95	15	90	23.0, 23.05, 23.0	100%
Using 10 cc. of Hydroxylamine Solution.					
12	3.84	7.5	65	9.2, 9.2	100%
13	2.92	15	65	9.2, 9.1	100%
14	2.33	15	65	9.2	100%
15	1.75	15	65	9.25, 9.25	100.5%
16	1.53	7.5	65	9.4	102%
17	1.45	15	65	9.45, 9.30	101 to 103%
18	1.40	8.5	50	11.3+	123+%
19[1]	1.40	8.5	50	9.6	104.4%
Using 25 cc. of Hydroxylamine Solution.					
20	1.08	7.5	91	24.2, 24.8	105–108%
Using 10 cc. of Hydroxylamine Solution.					
21	1.75	1	65	9.15, 9.15, 9.15	99.5%
22	1.75	1	65	9.1	99%
23	1.40	1	50	9.1, 9.05	98.8%
24[1]	1.40	1	50	9.1	99%
Using 25 cc. of Hydroxylamine Solution.					
25	1.08	2	80	23.6	102%

[1] In Expts. 19 and 24 the time of boiling was 30 minutes instead of 5 minutes.

Expts. 15 to 20 furnish clear evidence of a positive error when only a small excess of ferric sulfate is used. The results are irregular when only

40% or less excess ferric salt is used, and in one experiment (18) the permanganate end-point was not definite; in this case the titration was discontinued before a permanent color was obtained. In the companion experiment (19) with 30 minutes' boiling instead of 5 minutes the end-point was permanent. It was found by experiment that fleeting end-points (and high positive errors) were characteristic for experiments in which the reaction mixture was not heated, or was heated only to boiling. The error due to the small excess of ferric salt, therefore, is similar in character to that due to insufficient boiling in the standard procedure, and is doubtless due to the presence of hydroxylamine or nitroxyl when the permanganate is added. (See discussion earlier in paper.)

The results in Expts. 21 to 25, where the concentration of acid also is low, are more nearly correct; but this may be due to a compensation of the positive error resulting from incompleteness of the reaction and the negative error due to oxygen (which is favored by a low concentration of acid). To obtain further evidence the following experiments were performed in which the oxygen error was eliminated by adding 25 cc. of hydroxylamine solution from a pipet to the boiling ferric sulfate solution, as in Expt. 7(*c*). In Expts. 27 and 28, while no acid was added initially, in order that the permanganate titration might be made satisfactorily, 6 cc. of 6 *N* sulfuric acid was added to the hot solution after 5 minutes' boiling and just before the rapid cooling.

No.	Ferric sulfate referred to NH_2OH.	Cc. 12 *N* H_2SO_4.	Volume. Cc.	$KMnO_4$. Cc.	Titration result, % theoretical.
	Using 25 cc. of Hydroxylamine Solution.				
26	1.45	15	80	27.1	117%
27	1.45	0	75	22.95	99.8%
28	1.16	0	75	22.9	99.6%

The slight negative error in Expts. 27 and 28 indicates that the oxygen error was not quite completely eliminated, but they serve to show that the positive error is negligible when the ferric sulfate excess is small provided that the sulfuric acid concentration also is small. In other words, a high concentration of sulfuric acid retards the reaction, and the reaction can be completed in 5 minutes' boiling only when a very large excess of ferric sulfate is used. This conclusion is confirmed by the result of Expt. 26.

With regard to the relative merits of the two methods of making the ferric sulfate analysis, listed at the end of the preceding section, we are inclined to favor the first one, the regular procedure, since it has been more thoroughly tested. Also as noted in the preceding paragraph there seems to be a slight tendency towards a negative error in the second method.

Effect of the Presence of Chloride Ion.—While hydroxylamine sulfate was used throughout our experiments, it is certain that the ferric sulfate method is equally applicable to the analysis of hydroxylamine hydrochloride. Permanganate is not added until the final solution has been cooled and diluted, and the concentration of chloride ion will then be so small that there can be no appreciable reaction to form chlorine. Raschig's original experiments to test the method of analysis were made with hydroxylamine hydrochloride, and we also found that the addition of an amount of hydrochloric acid approximately equivalent to the hydroxylamine made no appreciable difference in the result.[1]

Analysis of the Gas Formed in Reaction 2.—At an early stage in this investigation, while we were still uncertain that hydroxylamine was quantitatively oxidized by the ferric ion to nitrous oxide, Mr. G. S. Parks undertook the analysis of the gas involved. He constructed an apparatus which enabled the hydroxylamine solution and the ferric sulfate-sulfuric acid solution to be mixed after the apparatus had been evacuated. Gas was evolved only very slowly at room temperature, but rapidly when the solution was heated to boiling. The gas was analyzed by adding excess hydrogen, burning and measuring the contraction; then adding excess oxygen, burning and measuring the contraction; absorbing the oxygen and measuring the residual nitrogen. The gas was found to be pure nitrous oxide within the experimental error. Three complete analyses gave 98.1, 99.9 and 100.0% nitrous oxide; a fourth analysis, based solely on the contraction with hydrogen, gave 101% nitrous oxide.

The Iodine Method.

The reaction between iodine and hydroxylamine in aqueous solution, as earlier investigations have shown, is rapid at low hydrogen ion concentration, *e. g.*, in the presence of sodium hydrogen carbonate or disodium phosphate. The rate is extremely slow in the presence of acid. Thus when 0.1 *N* iodine solution (in potassium iodide) was added drop by drop to 10 cc. of 0.1 *N* hydroxylamine sulfate solution, three drops (0.10 cc.) gave a color which persisted for several minutes; the minute amount of acid formed in the reaction with this amount of iodine gave a sufficient concentration of hydrogen ion practically to stop the reaction. In another experiment in 72 cc. of solution containing disodium phosphate and phosphoric acid in the proportion of 2 : 1, 0.06 cc. of iodine solution gave a distinct color. When in each of these experiments excess disodium phosphate solution was added, iodine was rapidly used up. Even in the phosphate solution, however, the reaction was not instantaneous near the end-point. On this account, after the preliminary experiments, the end-point was usually obtained by adding iodine solution in excess, usually

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[1] Cf. the recent experiments on the effect of the presence of chloride in the determination of nitrite by permanganate; Laird and Simpson, THIS JOURNAL, 41, 530 (1919).

about 5 cc. and after 3 to 5 minutes completing the titration with thiosulfate solution.

To remove the hydrogen ion formed in the reaction a phosphate solution was used which contained in one liter 0.1 mol of disodium phosphate and enough phosphoric acid to make the solution colorless when tested with phenolphthalein; the ratio of disodium phosphate to sodium dihydrogen phosphate in the solution was about 10 to 1. By using 200 cc. of this solution with 20 to 25 cc. of 0.1 *N* hydroxylamine sulfate the ratio of the monohydrogen and dihydrogen phosphates in the final solution was made about 2 : 1. Under these conditions there is no danger either of iodate formation, or of incomplete oxidation of hydroxylamine.

In our first experiments, even after elimination of the low results due to incomplete reaction (in the presence of too much acid), the results were extremely variable, the extremes differing by over 15%. As reported by other investigators, many factors were found to influence the results. When the total volume of the solution was large the results were relatively high, as Haga has pointed out. Increase of the concentration of iodide ion by the addition of potassium iodide tended to lower the results, although Haga had found that the presence of neutral salts, as sodium sulfate, caused high results. Increase of temperature, in the case of incomplete reaction, caused the reaction to proceed towards completion and thus raised the result; in other cases, however, low temperature seemed to favor high results. A very important factor was the method of adding the phosphate and iodine solutions,—including the order of mixing, and the time allowed. The results were very high when the phosphate and hydroxylamine solutions were mixed and the titration made by adding iodine to the mixture. Much lower results were obtained when the end-point was approached from the acid side, *e. g.*, by mixing iodine and hydroxylamine and gradually adding the phosphate solution, or by adding the iodine and phosphate solutions alternately.

When the hydroxylamine solution was accurately standardized by the two methods already described in this paper, and the theoretical results for the iodine titration compared with the actual data, it was found that the results described in the preceding paragraph as relatively high were definitely in error. For example, when 200 cc. of phosphate solution and 10 cc. of hydroxylamine solution were mixed at room temperature before any iodine was added, two determinations gave 21.33 and 21.22 cc. of 0.1 *N* iodine solution, while the theoretical result was 18.64 cc. Positive errors were the rule rather than the exception, at least when precautions were taken to ensure completeness of reaction.

The only definite source of error already known is nitrite formation, demonstrated by Haga. Since this involves oxidation of the nitrogen beyond the nitrous oxide stage, too much iodine must be used, and a positive error results. The conditions described above as favoring high results thus presumably favor nitrite formation.

We next developed an *empirical method* which gave theoretical results. To the hydroxylamine solution in an Erlenmeyer flask was added an excess of 0.1 *N* iodine solution from a pipet or buret; 40 cc. of phosphate solution was added from a buret in 5 cc. portions at 2-minute intervals and then the remaining 160 cc. of phosphate solution was added; after 5 minutes the excess iodine was titrated with 0.1 *N* thiosulfate solution. It was observed that the reaction between hydroxylamine and iodine was nearly completed by the time the 40 cc. of phosphate solution had been added. In one set of experiments with 10 cc. of 0.1864 *N* hydroxylamine solution, while the theoretical result was 18.64 cc. of 0.1 *N* iodine solution, the following results were obtained: 18.78, 18.56, 18.58, 18.71, 18.66, 18.60 and 18.46 cc. of 0.1 *N* iodine solution. Thus the results are reproducible, but only when the prescribed conditions are maintained.

The question arose as to whether this method gave correct results only because there was a compensation of errors. Direct evidence was finally obtained by determining accurately the amount of nitrite in the final solution. Nitrite was always found; and since this implies a positive error there must have been an as yet undiscovered compensating negative error.

The method used in the *determination of nitrite* in the presence of phosphate and iodide was that developed independently by Chabrier[1] and by Raschig[2] which has recently been tested by Davisson.[3] It depends upon the fact that nitrite does not react with iodide in neutral solution, but is quantitatively reduced to nitric oxide in the presence of acid; the liberated iodine is titrated with thiosulfate solution after 2 minutes. Air is excluded by means of carbon dioxide, since otherwise nitric oxide would react with oxygen, the product would be reduced by iodide, and the formation of iodine would continue due to continued repetition of this cycle. The presence of nitrous oxide has no effect since nitrous oxide does not oxidize iodide ion in acid solution.

In analyses made by the empirical method with 25 cc. of hydroxylamine sulfate solution, the theoretical value is 25.16 cc. of 0.1 *N* iodine solution, but the final solution was found to contain enough nitrite to liberate 0.60 to 0.70 cc. of iodine when the nitrite was reduced to nitrous oxide. This would correspond to a positive error in the iodine titration of 1.2 to 1.4 cc. of 0.1 *N* iodine solution (the amount being doubled since

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[1] Chabrier, *Encyclopédie chimique*, **4**, 262 (1888); see Wiley, *Princ. and Pract. of Agric. Anal.*, 2nd Ed., II, 474 (1908).

[2] Raschig, *Ber.*, **38**, 3911 (1905).

[3] Davisson, THIS JOURNAL, **38**, 1683 (1916).

the theoretical result is based on the quantitative formation of nitrous oxide), which is an error of about 5%.

The final solution after the iodine titration might also contain nitroxyl, and it was therefore necessary to devise a method of eliminating this substance. From Raschig's work and our own experiments with the ferric sulfate method it seemed certain that this could be done by boiling the final solution. The effect of boiling on the nitrite method was accordingly determined. It was found that a mixture of nitrite, iodide, and 200 cc. phosphate solution could be boiled for 5 minutes without appreciable loss of nitrite. However, when a solution containing tetrathionate, iodide, and phosphate was boiled an appreciable amount of a reducing agent was formed, and the quantity continued to increase with continued boiling. The reducing agent was determined by titration with iodine; after several hours' boiling the formation of reducing agent was still continuing, although the amount of iodine that had been used was over twice that necessary to form the original amount of tetrathionate from thiosulfate; no sulfur was precipitated.

Since it was evidently impossible to boil any final solution (after the iodine titration of hydroxylamine) which contained tetrathionate, some experiments were performed in which sulfurous acid was used instead of thiosulfate. The sulfurous acid titration was the basis of the original Bunsen method of determining iodine, and is reliable provided the sulfurous acid solution is standardized each day before use. However, the titration was found to be unreliable in the presence of our phosphate solution; too much sulfurous acid was used, and errors of more than 10% were observed. When the phosphate solution, after this titration, was boiled for 5 minutes no reducing agent was formed. Accordingly sulfurous acid was used simply to remove the excess of iodine in the hydroxylamine determination; analyses were made by the empirical method, with 25 cc. of hydroxylamine solution as in the experiments described in the preceding paragraph; the final solution was boiled for 5 minutes, and cooled under carbon dioxide; the amount of nitrite was found to be practically the same as before. It follows that, in the empirical iodine method for determining hydroxylamine, nitrite is formed corresponding to a positive error of about 5%, and that there must be a compensating negative error.

Before describing our final experiments the results of a number of experiments will be described in which the final solution after the iodine titration was acidified with sulfuric acid in the presence of air. The same behavior was observed as in blank experiments with nitrite in the presence of the phosphate solution; the formation of iodine was rapid at first and was continuing only very slowly after 24 hours. In the experiments by the empirical method, similar to those in which nitrite was determined, after 24 hours the amount of iodine liberated in the acidified solution was equal to 10 to 16 cc. of 0.1 *N* iodine. This was not greater than was to be expected for the amount of nitrite known to be present. Also when the solution was again made approximately neutral by the addition of a large amount of solid disodium phosphate, hydroxylamine was found to be absent. There is therefore no evidence that the formation of nitroxyl from hydroxylamine by means of iodine is a reversible reaction. Before the nitrite experiments were performed we had thought that the large amount of iodine formed on the addition of acid was due, in part at least, to a reaction between nitroxyl, iodide ion and hydrogen ion.

The negative error referred to in the paragraphs just before the preceding one was proved to be due to the presence of oxygen of the air. This error appears to be absent when the hydrogen ion concentration is very low throughout the reaction between hydroxylamine and iodine, *e. g.*, when the phosphate solution is added before the iodine. Any nitrite formed remains in the solution unchanged, since it cannot react with iodide ion under these conditions. On the other hand, this error is encountered when the phosphate solution is added slowly to the hydroxylamine-iodine solution, as in the empirical method. It seems probable that the hydrogen ion concentration is then large enough to permit of some reaction between the nitrite and iodide; the nitric oxide formed is oxidized by oxygen and the product is reduced, with the result that some iodine is liberated due to the presence of oxygen. According to this theory the correctness of the empirical method depends upon the time allotted for the addition of the phosphate solution, and it is to be predicted that low results will result if this time is increased. The following experiments were performed by the empirical method of analysis, except that in the second and third experiments, after 30 cc. of phosphate solution had been added, the mixture was allowed to stand in contact with air for 1 and 12 hours, respectively.

25 cc. of Hydroxylamine Solution = 23.16 cc. of 0.1 *N* Iodine Solution.

Time of interruption after addition of 30 cc. phosphate.	Result of titration. Cc. of 0.1 *N* iodine solution.	Nitrite determination. Cc. of 0.1 *N* iodine solution.
2 min	23.2	0.7
1 hour	22.1	0.6
12 hours	21.0	0.25

The results, in the second column, are distinctly low in the second and third experiment, as was expected. It is interesting to note that the nitrite also decreased with time, which also favors the theory outlined above. Two additional experiments were performed by the empirical method but in the presence of carbon dioxide. In the first experiment, in which the air was only partially eliminated, the final result was 23.3 cc. of 0.1 *N* iodine solution, and the nitrite determination 0.6 cc. of iodine solution. In the second experiment, where the exclusion of air was more satisfactory, the final result was 23.5 cc. of iodine solution, and nitrite 0.55 cc. of iodine solution. Thus when the amount of air is decreased the titration results are somewhat higher.

The iodine method therefore seems to be of little value. The empirical method gives correct results only on account of a compensation of the positive error due to nitrite by the negative error due to oxygen. Nitrite is formed under widely different conditions, and it seems scarcely worth while to continue the search for conditions in which the oxidation to nitrous oxide will be quantitative.

Reaction of Iodine and Thiosulfate in Disodium Phosphate Solution.

As a result of the observation of the instability of tetrathionate in the hot phosphate solution, referred to above, some experiments were performed on the reaction between iodine and thiosulfate in the presence of phosphate. It is recalled that our disodium phosphate solution contained a small proportion of sodium dihydrogen phosphate.

When the iodine-thiosulfate titration was made in this solution at room temperature an error of about 1% was observed, in the direction that too much iodine was used.[1] This error was eliminated if enough acid was first added to the phosphate solution to convert the disodium phosphate into a mixture of sodium dihydrogen phosphate and phosphoric acid. It is to be noted that in the hydroxylamine determination, since thiosulfate was used to determine the small excess of iodine added, a slight positive error was thereby introduced. It was negligible, however in comparison with the large positive error due to nitrite.

Three experiments on the reaction between iodine and thiosulfate in disodium phosphate solution at a higher temperature were made for us by Miss Jennie Clauson in this laboratory. 8.8 cc. of 0.1 *N* thiosulfate solution, somewhat more than an eightfold amount of iodine in potassium iodide solution, water, and 18 g. of $Na_2HPO_4.12H_2O$ were placed in 100 cc. Pyrex glass tubes, the tubes were sealed and heated at 70 to 90° in a water-bath for about one hour. The excess iodine was determined at room temperature by titration with thiosulfate.

Expt. No.	1.	2.	3.
Temperature (approx.)	70°	70°	90°
Cc. Thiosulfate Solution Equivalent.			
Iodine solution	79.6	79.6	79.6
Iodine excess	10.5	10.55	8.6
Iodine used	69.1	69.05	71.0
$^1/_8$ iodine used	8.64	8.63	8.87
Thiosulfate solution used	8.8	8.8	8.8

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[1] That iodate was not formed was proved by acidifying the final solution with H_2SO_4; there was no liberation of iodine at once.

Within the limits of the experimental error the amount of iodine used is 8 times that required to oxidize the thiosulfate to tetrathionate. It is obvious that there is quantitative oxidation to sulfate.

$$S_2O_3^{--} + 4I_2 + 5H_2O = 2SO_4^{--} + 8I^- + 10H^+.$$

While the corresponding reactions with excess bromine and chlorine are well known, we have as yet found no reference to this reaction for iodine.

Quantitative Oxidation of Hydroxylamine to Nitrate.

The work of Knorre and Arndt[1] shows the scarcity of quantitative reactions when hydroxylamine is treated with oxidizing agents. On this account it is interesting to note that Rupp and Maeder[2] have recently demonstrated the quantitative oxidation of hydroxylamine to nitrate in acid solution by excess of a bromate-bromide mixture or of a hypobromite-bromide mixture. Since bromine can be formed in both cases it seems certain that bromine will have the same effect.

Early in the present investigation we made a few experiments on the reaction between hydroxylamine and hypochlorous acid, the latter in small excess over that necessary for oxidation to nitrate assuming reduction of hypochlorous acid to chlorine. Precautions were taken to prevent loss of chlorine, and the total amount of oxidizing agent that remained after a few minutes was determined by adding potassium iodide and titrating the iodine formed with thiosulfate. The amount of hypochlorous acid used in this reaction was found to vary between 90 and 97% of that calculated for oxidation of hydroxylamine to nitrate. It seems not improbable that conditions could be found in which this reaction would be quantitative, but we have not had an opportunity to continue these experiments.

Summary.

Three methods for the determination of hydroxylamine have been investigated: (1) the reduction of hydroxylamine to ammonium salt by excess titanous salt in acid solution, (2) the oxidation to nitrous oxide by excess ferric sulfate in sulfuric acid solution, with titration of the ferrous salt by permanganate solution, and (3) the oxidation to nitrous oxide by iodine in a solution kept neutral by means of sodium monohydrogen phosphate.

The titanous salt and ferric salt methods were found to be accurate, but the iodine method was unsatisfactory.

In addition to the known positive error in the ferric salt method, which is due to the addition of permanganate while some hydroxylamine or an intermediate product, nitroxyl, is still present, a negative error due to oxygen of the air was found under certain conditions. Both errors are easily avoided.

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[1] Knorre and Arndt, *Ber.*, **33**, 30 (1900).

[2] Rupp and Maeder, *Arch. Pharm.*, **251**, 298 (1913).

In the iodine method three errors were encountered: (1) that due to incomplete reaction, which is avoided by the addition of disodium phosphate, (2) nitrite formation which occurs under all the conditions investigated and corresponds to a positive error, and (3) absorption of oxygen of air, which corresponds to a negative error. An empirical method was developed for obtaining theoretical results, but it was shown to be correct only on account of compensation of errors (2) and (3).

Hydroxylamine is oxidized mainly to nitrate by hypochlorous acid solution in excess.

In a disodium monohydrogen phosphate solution thiosulfate can be oxidized quantitatively to sulfate by iodine. The reaction is rapid at 70°.

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NOTES.

Corrections.—"*A New Theory Relating Constitution to Taste.*" The following corrections should be made in the article which appeared under this title in the June issue:[1]

P. 859, first formula on third line, $CO_2H.CHNHCH_3$-(H), and first formula on 5th line, $CH_2OH.CH_2.CHOH$-(H). The (H) should be omitted in both cases.

P. 859, in line 7, formula CHONO-(H) should read CH_2ONO-.

P. 860, classification of auxoglucs. Formula given under (3), C_nH_{2n+10} should read $C_nH_{2n+1}O$, and formula under (4), C_nH_{2n+10n} should read $C_nH_{2n+1}O_n$.

P. 861, formula of serine, $CH_3OH_2CHNH_2CO_2H$, should read $CH_2OH.$-$CHNH_2.CO_2H$.

P. 663 and 664. In Tables I, II and III, last line, the formula of the auxogluc should read in each case $C_nH_{2n+1}O_n$.

P. 867, under (2) the fifth formula, $C^{H_2-x}_{H1_x}$—, should read $C^{H_3-x}_{H1x}$—.

P. 867, (3), the first formula under (*b*), $C_nH_{2n+1}O$, should read C_nH_{2n+1}, and the first formula under (*d*), $C_nH_{2n-1}O_n$, should be $C_nH_{2n+1}O_n$.

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Rollin G. Myers.

Correction.—The omission of certain lines from Table III of my paper, in the July Journal,[2] on "The Activities of the Ions of Strong Electrolytes" makes the material there presented difficult for a reader to interpret. The activity ratios (Cols. 9 and 10) refer to the pairs of concentrations of hydrochloric acid and potassium chloride given in Cols. 4 and 5. A correct version of the table appears below.

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[1] This Journal, 41, 855 (1919).

[2] *Ibid.*, 41, 1089 (1919).