Summary

In this article a volumetric method for the determination of sulfur has been described. Sulfur has been determined thermometrically by titrating the sample at room temperature with a standard solution of barium chloride. To obtain the end-points, temperature increments are plotted against volumes. It has been noted that the barium chloride solution should be standardized thermometrically against a material similar to that to be analyzed. This latter point has not, however, been thoroughly investigated.

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

THE OXIDATION OF HYDRAZINE. I. THE VOLUMETRIC ANALYSIS OF HYDRAZINE BY THE IODIC ACID, IODINE, BROMINE, AND HYPOCHLOROUS ACID METHODS

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Introduction

While numerous methods for the analysis of hydrazine, N_2H_4, have been proposed, all of which depend upon its oxidation to nitrogen, Browne and Shetterly[1] have shown in many cases that some ammonia and hydronitric acid (or ammonia alone) are formed in addition to nitrogen, and that the amounts of these by-products can often be greatly increased by a suitable variation of the experimental conditions. The further study of the accuracy of methods of determining hydrazine, which was evidently necessary, was begun by Hale and Redfield[1] in 1911.

The methods suggested have usually been nitrometric, that is, the nitrogen evolved is collected and measured. In some cases the corresponding oxidimetric method has been used, in which a known amount of oxidizing agent in excess of 4 equivalents per mole of hydrazine is used and this excess determined by titration. However, we have found in the literature only two oxidimetric methods[2,3] which are rapid, and which at the same time seem to be accurate within 0.2% on the basis of published experimental evidence. These will be referred to later.

We have investigated the accuracy of a number of rapid oxidimetric methods. In order to detect possible side reactions we have examined

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[1] Browne and Shetterly, THIS JOURNAL, (a) (I) **29,** 1305 (1907); (b) (II) **30,** 53 (1908); (c) (III) **31,** 221 (1909); (d) (IV) **31,** 783 (1909). The various analytical methods are surveyed in these articles from the Cornell Laboratory, and in the fifth article of the series, (e) (V) Hale and Redfield, *ibid.*, **33,** 1353 (1911).

[2] Jamieson, *Am. J. Sci.*, [4] **33,** 352 (1912).

[3] Kurtenacker and Wagner, *Z. anorg. allgem. Chem.*, **120,** 261 (1922).

the effect of variations in the experimental conditions, such as: the order and speed of mixing the reagents, and the relative amounts and concentrations of the reagents used. Side reactions seem most likely to occur when the oxidizing agent is added very slowly to the hydrazine, that is, when the hydrazine is present in excess during the reaction; this is in general agreement with the results of Browne and Shetterly.

In the present article four rapid methods are described, which agree among themselves to within 0.2%, and do not show appreciable variations with the experimental conditions. It may, therefore, be concluded that in these cases the hydrazine is quantitatively oxidized to nitrogen. While the reactions involved have been discussed in the literature, the methods of analysis here recommended are essentially new. The experimental work was completed in May, 1922.

The Iodic Acid Method

Experimental.—When it was found, in preliminary experiments, that the iodate-hydrazine reaction, although rather slow in dilute neutral or alkaline solutions at room temperature, is very rapid in acid solution, the latter condition was chosen for the analytical method to be tested. Excess of iodic acid was taken; after the completion of the reaction, excess of potassium iodide was added and the total iodine determined (both that liberated during the hydrazine-iodic acid reaction, and that during the iodide-iodic acid reaction). The reactions are:

$$5N_2H_6^{++} + 4IO_3^- = 5N_2 + 2I_2 + 6H^+ + 12H_2O \qquad (1)$$

and

$$5I^- + IO_3^- + 6H^+ = 3I_2 + 3H_2O \qquad (2)$$

Since the rate of reaction between iodine and hydrazine is slow in acid solution, it is evident that iodic acid must be present in the solution when potassium iodide is added to determine the excess oxidizing agent. As shown in the above equations, iodic acid is reduced to iodine by both hydrazine and iodide. The iodine is subsequently reduced to iodide by the thiosulfate, and it follows that more than six-fifths of the amount of iodic acid calculated on the basis of reduction to iodide must be used to insure the presence of excess of iodic acid in the first stage.

The hydrazine solution was a stock solution of hydrazine sulfate, which was also used in our experiments with several other methods, and was approximately 0.11 *M*. The iodic acid solution was made from iodic anhydride prepared according to the method of Lamb, Bray, and Geldard.[4] It was standardized against thiosulfate after the addition of acidified potassium iodide in excess and was found to be 0.1219 *N* as an oxidizing agent being reduced to iodide (that is, 0.0203 *M*). The thiosulfate solution was standardized against a stock permanganate solution after the latter had been treated with acidified potassium iodide in excess,[5] and was found to be 0.1006 *N*. Finally, the permanganate itself was standardized against Bureau of Standards sodium oxalate.

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[4] Lamb, Bray, and Geldard, This Journal, **42**, 1636 (1920).

[5] This method was chosen because it is rapid and gives reproducible results. Recent work in this Laboratory has furnished evidence that it is accurate within 0.1 to 0.2%.

The standard procedure recommended is as follows. To 10 cc. of 6 *N* sulfuric acid in a ground-glass-stoppered flask add a measured[6] amount of 0.1 *N* iodic acid 30 to 50% in excess of that needed to oxidize the hydrazine, and finally add the hydrazine. After five minutes add potassium iodide in excess and titrate the iodine with thiosulfate solution.

Table I gives the results.

Table I

The Iodic Acid Method

The volume of iodic acid (calc. as 0.1 *N*) was 56.00 cc. in each experiment except 1–5 in which 39–53 cc. was used and Expt. 18 in which 112 cc. was used.

Expt.	Volume of N_2H_4 Cc.	Volume of thio. calc. as 0.1 *N*	Calcd. *M* of N_2H_4	Time in min.	Total volume Cc.	Approx. acid concn. *N*
1–5	6.88	...	0.1104–6	10	50	...[a]
6	9.33	14.85	.1104	10	75	1.0
7	9.33	14.85	.1104	10	75	1.0
8	9.97	12.02	.1104	2	75	1.0
9	9.97	12.00	.1104	2	75	1.0
10	9.95	12.14	.1103	3	75	1.0
11	9.95	12.32	.1098	1	75	1.0
12	9.95	12.22	.1101	20	75	1.0
13	9.95	12.24	.1100	3	100	2.0
14	9.95	12.35	.1097	3	100	0.3
15	6.88	25.75	.1100	3	100	1.0
16	6.88	25.72	.1101	3	100	1.0
17	6.88	25.65	.1103	3	100	1.0[b]
18	6.88	81.77	.1102	3	120	0.5
19	6.88	25.71	.1101	3	60	1.0[c]
20	9.95	12.15	.1102	48 hrs.	300	1.0

Concentration of the hydrazine sulfate solution, 0.11025 ± 0.15%.

[a] Preliminary values.

[b] The hydrazine was added first.

[c] Done two months later.

Variation of the Experimental Conditions.—For acid concentrations from 0.5 *N* to 2.0 *N* there is no evidence of a variation of the results, but at a lower concentration, 0.3 *N* in Expt. 14, the low result indicates that the hydrazine-iodate reaction is not quite complete within three minutes. The time allowed for completion of this reaction was varied between one minute and 48 hours. When the acid concentration is 1 *N*, one minute is too short a time (see Expt. 11), but a time of three minutes seems to be sufficient (see Expts. 10, 15 and 16).

The order of addition was found to be immaterial. In the experiments tabulated the iodic acid was introduced before the hydrazine, except in Expt. 17, where the reverse was true. In this experiment and others not given in the table the concentration of hydrazine was found to be the same

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[6] All burets, pipets and measuring flasks were calibrated.

as in those done according to the standard procedure. In fact, in a series of experiments in which the iodic acid was added drop by drop to the hydrazine, the total time involved being about 27 minutes, the results agreed with that obtained in the standard procedure within 0.1%. As has already been stated in the introduction, this fact shows that at room temperature the iodic acid-hydrazine reaction is inherently a smooth, quantitative reaction free from side reactions.

The excess of iodic acid used is also immaterial. In our experiments the excess of iodic acid (above that required for reduction to iodine and therefore in addition to the six-fifths already mentioned) was in general between 5% and 20%. In Expt. 18, where a 200% excess was used, an identical titer was obtained.

In some experiments not listed in Table I, exactly the same results were obtained in an atmosphere of carbon dioxide as in the presence of air. It follows that the presence of atmospheric oxygen has no effect on the results of this method.

In Expt. 19, which was done more than two months after the rest, the hydrazine concentration was unchanged, showing that a solution of pure hydrazine sulfate, which is acid due to hydrolysis, is not oxidized appreciably during that interval of time by the oxygen of the air.

Historical.—Rimini,[7] who was the first to recommend the use of iodate in analyzing hydrazine, added an excess of potassium iodate to the hydrazine salt, boiled the mixture until the iodine was completely expelled, and measured either the volume of nitrogen formed or the excess of iodate that remained. Though acid was not added it was formed during the reaction, as is shown in Equation 1. He gave no experimental data, but stated that he had proved the reaction to be complete and free from side reactions. His statements were confirmed by the careful investigation of Hale and Redfield.[1] These authors give detailed directions and results, and state that the chief disadvantage of the method lies in the length of time (30 minutes) required for the expulsion of the iodine. As we have seen above, this disadvantage is removed in our method.

When iodate is treated with an excess of hydrazine in acid solution the iodine that is first formed is reduced to iodide,[8] although rather slowly. The final result is represented by the equation

$$3N_2H_4{\cdot}H_2SO_4 + 2KIO_3 = 3N_2 + 2KI + 6H_2O + 3H_2SO_4 \qquad (3)$$

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[7] Rimini, *Gazz. chim. ital.*, **29**, I, 265 (1899). See also Riegler, *Z. anal. Chem.*, **40**, 92 (1901).

[8] Riegler, *Z. anal. Chem.*, **41**, 17, 413 (1902); **46**, 315 (1907). Schlötter, *Z. anorg. Chem.*, **38**, 184 (1904). Jannasch and Jahn, *Ber.*, **38**, 1576 (1905). On the basis of this reaction Riegler has devised nitrometric methods for the indirect determination of carbonate, sulfate, hydroxide and iodide.

Browne and Shetterly[9] have shown that neither ammonium ion nor hydronitric acid is formed under these conditions, although both of these substances were formed in the corresponding reaction of bromic or chloric acid with an excess of hydrazine. They attribute the absence of side reactions in the case of iodate to the presence of the free halogen, since considerable quantities of ammonium ion and hydronitric acid were found when the formation of iodine was prevented by the presence of silver sulfate during the reaction. This complication resulting from the addition of a silver salt illustrates the necessity of demonstrating that a hydrazine reaction is quantitative under the conditions actually employed in the analysis.

Rimini,[10] in a second article, recommended a method (either nitrometric or oxidimetric) for the determination of hydrazine based on Reaction 3 in alkaline solution in the presence of an excess of iodate, but did not give any test analyses or state the time allowed and the temperature. These experimental conditions are important since the iodate reaction is rather slow in alkaline solution at room temperature. Furthermore, it is not unlikely that side reactions, although absent in acid solution, may appear in the alkaline solution.[11]

[9] Ref. 1b, pp. 59 and 62.

[10] Rimini, *Atti. accad. Lincei,* [5] **15,** II, 320 (1906).

[11] That this is the case has since been found by the following experiments of L. R. McMaster in this Laboratory. The thiosulfate solution used was approximately 0.1 *N*. It was not necessary to standardize it accurately, since only comparative results were desired on the iodate methods in acid and alkaline solutions. 1 cc. of the iodic acid solution used was found to be equivalent to 1.252 cc. of the thiosulfate solution by the usual iodimetric method. A 4.95cc. portion of a stock hydrazine sulfate solution was used in all the experiments. In six analyses by the standard iodic acid method, with 40–50 cc. (accurately measured) of the iodic acid solution, this was found to be equivalent to 34.00–34.05 (av. 34.02) cc. of the sodium thiosulfate solution.

In all experiments in alkaline solutions lower results were obtained. Ten cc. of 0.868 *N* sodium hydroxide solution and the iodic acid solution were mixed and the hydrazine sulfate was added; after a definite time an excess of potassium iodide and 10 cc. of 6 *N* sulfuric acid were added, and the free iodine was titrated with thiosulfate. Some of the results are tabulated below.

Expt.	Volume HIO_3 Cc.	Volume alkaline solution Cc.	Time Min.	Thiosulfate equivalent to hydrazine Cc.
1	34.81	50	10	33.34
2	29.88	45	10	33.31
3	29.88	45	6	32.89
4	29.88	45	2	32.55
5	29.88	45	1/2	27.07
6	29.88	145	1/2	11.82

The highest results obtained are still over 2% too low. As we shall see later, this error is probably due to the action of oxygen on hydrazine in alkaline solution. Another source of error is the slowness of the reaction between iodate and hydrazine in alkaline solution. This may be very large in dilute solution when only a short time is allowed for the reaction (see Expt. 6).

Andrews' method[12] of titrating with an iodate in the presence of concd. hydrochloric acid has been applied by Jamieson[2] to the determination of hydrazine, and tested by the analysis of hydrazine sulfate and other hydrazine salts. The reaction

$$N_2H_6SO_4 + KIO_3 + 2HCl = N_2 + ICl + 3H_2O + 3H_2O + KCl + H_2SO_4 \qquad (4)$$

is rapid; the end-point, which depends on the presence of a small amount of chloroform, is sharp; and there is no reason to doubt the accuracy of the method. It has been accepted as correct by Kurtenacker and Wagner[8] in their recent investigation of the bromic acid-bromide method for the determination of hydrazine.

The Iodine Method

Experimental.—The reaction between iodine and hydrazine

$$N_2H_6SO_4 + 2I_2 = N_2 + H_2SO_4 + 4HI \qquad (5)$$

was investigated in alkaline solution, since it is rapid under this condition, and is slow in acid solution. The order of mixing the reagents adopted in the analytical method was hydrazine-iodine-alkali (H-I-A). The alkali was added last for two reasons. When iodine and alkali are mixed, iodate is formed fairly rapidly; and an error may result which is equivalent to the use of an insufficient amount of the oxidizing agent. When hydrazine and alkali are allowed to stand in the presence of air[13] the hydrazine slowly decomposes, and the method again yields low results.

The standard procedure was as follows. The hydrazine solution was pipetted into a ground-glass-stoppered flask, a measured excess of iodine was then added with a pipet, and finally excess of alkali was introduced. After two minutes the solution was acidified, and the excess of iodine determined with thiosulfate.

The iodine solution (in potassium iodide) was standardized against the reference permanganate. Table II gives the results.

Variation of Experimental Conditions.—The first 14 experiments, in which the standard order of mixing was followed, show no variation from the average greater than 0.2%. While in general the amount of sodium hydroxide added was sufficient to make the final concentration of alkali 0.05 to 0.1 *N* (after Reaction 5 had taken place), this concentration was only 0.008 *N* in Expt. 1 and was as high as 0.5 *N* in Expt. 5; the low result in Expt. 20 is due to the fact that an insufficient amount of sodium hydroxide was added. The excess of iodine used was about 3% in one group of experiments and 50% in the other. The time of two minutes

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[12] Andrews, This Journal, **25,** 756 (1903).

[13] We have found that in the absence of air the decomposition of an alkaline solution of hydrazine at room temperature is inappreciable within a period of 24 hours. It follows that the "decomposition" ordinarily observed is due to a reaction between hydrazine and oxygen, and that much of the work on the reactions of hydrazine in alkaline solution should be repeated in the absence of oxygen.

usually allowed for the reaction was extended to eight minutes in Expt. 9, and to over half an hour in Expt. 2.

TABLE II

THE IODINE METHOD

The volume of hydrazine used was 6.88 cc. in Expts. 6, 7, 8, 11–15, 17 and 9.95 cc. in all others. The volume of iodine (calc. as 0.1 *N*) was 45.563 cc. in all experiments.

Expt.	Volume of thio. calc. as 0.1 *N*	Calculated concn. of hydrazine	NaOH added Cc.	Order of mixing
1	1.70	0.1102	75 (0.1 *N*)	H-I-A
2	1.69	.1102	Excess	H-I-A
3	1.65	.1103	10 (1 *N*)	H-I-A
4	1.79	.1100	10 (1 *N*)	H-I-A
5	1.62	.1104	75 (1 *N*)	H-I-A
6	15.24	.1102	Excess	H-I-A
7	15.18	.1104	Excess	H-I-A
8	15.19	.1104	Excess	H-I-A
9	1.68	.1103	Excess	H-I-A
10	1.78	.1100	Excess	H-I-A
11	15.28	.1101	Excess	H-I-A
12	15.26	.1101	Excess	H-I-A
13	15.28	.1101	Excess	H-I-A
14	15.25	.1102	Excess	H-I-A
15	15.23	.1102	10 (1 *N*)	A-I-H[a]
16	12.19	.0840	10 (1 *N*)	A-I-H
17	15.32	.1099	10 (1 *N*)	A-I-H
18	1.87	.1098	Excess	H-A-I[b]
19	2.62	.1079	Excess	H-A-I[c]
20	2.38	.1085	50 (0.1 *N*)	H-I-A[d]

Concentration of hydrazine sulfate solution (Expts. 1 to 14), 0.1102 *M* ± 0.2%.

[a] 100 cc. of water added.

[b] Waited one-half minute before adding KI_3.

[c] Waited ten minutes before adding KI_3.

[d] 23% less than the calculated amount of alkali was used.

Expts. 15 to 19 are chosen from a set of over 15 experiments to illustrate the effect of varying the order of mixing the reagents. When the alkali and iodine are mixed before the hydrazine is added, the error due to iodate formation is large if the excess of iodine is small (Expt. 16), and becomes smaller as the excess of iodine is increased (Expt. 17). Indeed, this error may be completely eliminated (Expt. 15) by the use of a 50% excess of iodine and the addition of water to slow down the iodate formation.

The error due to loss of hydrazine when the alkali and hydrazine are mixed increases with the time allowed before the addition of the iodine solution (compare Expts. 18 and 19), but may be made very small by adding the iodine as quickly as possible. In other experiments not recorded in the tables it was found that 0.9% of the hydrazine disappeared within five minutes and about 20% in 16 hours when the solution was approximately 0.5 N with respect to alkali and 0.05 M with respect to hydrazine; in these cases the hydrazine was determined by the bromine method, as described below.

Historical.—Browne and Shetterly[14] showed that hydronitric acid is not formed in the reaction between iodine and hydrazine either in acid or alkaline solution, and (as noted above) that the presence of iodine in the iodic acid reaction probably prevents the formation of ammonium ion and hydronitric acid. These results indicated that the iodine hydrazine reaction should yield an accurate analytical method.

Stollé[15] had already determined hydrazine by direct titration with 0.1 N iodine, after the addition of sodium bicarbonate as a buffer. The reaction is slow near the end-point, and the last portion of iodine was added slowly, drop by drop, until a permanent starch-color was obtained. The time required lessens the value of this iodine method. While Stollé was able to obtain reproducible results, Rupp[16] reported that he had previously found that this method gave irregular results. He recommended the use of sodium potassium tartrate or sodium acetate as the buffer, the addition of excess of iodine, and the titration of the excess after 15 minutes. Direct titration was impossible because in these buffer solutions (on account of the greater acidity) the reaction was still slower than in the bicarbonate solution. Both Stollé and Rupp checked their methods by test analyses with hydrazine sulfate, but the following discrepancy may be noted. Stollé stated that hydrazine in bicarbonate solution slowly decomposes[17] while Rupp used as his stock solution for the test analyses a solution of hydrazine in sodium bicarbonate.

The Bromine Method in Acid Solution

Experimental.—After a number of satisfactory preliminary experiments the results presented below were obtained within a period of two days with a single stock solution of bromine, the concentration of which remained constant within 0.1%. This solution was stored in a large glass flask provided with a siphon tube outlet sealed into the neck of the container. To decrease the vapor pressure of bromine, enough potassium bromide was added to make the bromide concentration about 0.5 M. Samples were withdrawn by siphoning into an automatic pipet so arranged that it could be filled without danger of loss of bromine. The solution was standardized each day by adding an excess of potassium iodide and a little sulfuric acid, and titrating with thiosulfate solution.

The standard procedure adopted was as follows. To 9.33 cc. of hy-

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[14] Ref. 1b, p. 61.

[15] Stollé, *J. prakt. Chem.*, [2] **66**, 332 (1902).

[16] Rupp, *ibid.*, [2] **67**, 140 (1903).

[17] We have obtained similar results in a phosphate solution in which the hydrogen-ion concentration was approximately 10^{-7}; Table IV, nos. 4, 10, 11.

drazine sulfate solution pipetted into a ground-glass-stoppered flask containing 10 cc. of 6 N sulfuric (or no acid at all, as the case may be) was added a constant amount of bromine solution (86.71 cc.). After two minutes an excess of potassium iodide (and acid if the solution had not been originally acidified) was added, and the liberated iodine titrated with thiosulfate solution.

Table III gives the results.

In Col. 4 is shown the time interval, T_1, between the mixing of the reagents and the addition of potassium iodide; the figures in brackets, T_2, given in a few cases, refer to the time interval between the addition of the iodide and the titration with thiosulfate. In Col. 5, which gives the order of mixing, Ac stands for acid, H for hydrazine, and B for bromine.

TABLE III

THE BROMINE METHOD IN ACID SOLUTION

9.33 cc. of hydrazine and 84.06 cc. of bromine calcd. as 0.05 N were used in each experiment.

Expt.	Volume of thio. calc. as 0.1 N	Calcd. concn. of N_2H_4	Time Minutes	Order of mixing
1	1.06	0.1098	2	Ac-H-B
2	1.01	.1099	2	Ac-H-B
3	1.03	.1099	2	Ac-H-B
4	0.89	.1102	15 (T_2 = 2)	Ac-H-B
5	.90	.1102	0 (T_2 = 2)	Ac-H-B
6	.90	.1102	2 (T_2 = 0)	Ac-H-B
7	.94	.1101	2 (T_2 = 15)	Ac-H-B
8	.99	.1100	2	H-B
9	.89	.1102	2	H-B
10	.99	.1100	2	Ac-H-B
11	.89	.1102	2	Ac-H-B
12	.91	.1102	2	B-Ac-H
13	.89	.1102	2	H-Ac-B

Concentration of hydrazine sulfate solution, 0.1101 M ± 0.2%.

Variation of Experimental Conditions.—A variation of the time allowed for the reaction (T_1) between 0 and 15 minutes had no effect on the results; the reaction between bromine and hydrazine is therefore very rapid in the dilute acid solution. The following variations in the acidity were without influence: in Expts. 8 and 9 the only acid present was that produced in the reaction, in Expt. 11, 100 cc. of 2 N sulfuric acid were used, and in the remaining experiments 10 cc. of 6 N sulfuric acid. That the order of mixing the reagents is immaterial is shown by the results in Expts. 12 and 13, in which the order is different from that in the remaining experiments.

The volatility of the bromine seems to be the only source of error in this method. As we have shown, this error can be avoided while mixing the reagents, and is negligible when the excess of bromine is small (2% in the above experiments); but it is probably appreciable when the bromine excess is large, since the nitrogen evolved then carries bromine out of the flask. Our results on the magnitude of this error are not conclusive, but two experiments with 38% excess of bromine (6.88 cc. of the hydrazine solution) indicated that it might be as large as 0.5%.

Historical.—After this investigation had been completed Kurtenacker and Wagner[3] described a method based on the oxidation of hydrazine by excess of a mixture of either bromate, bromide and hydrochloric acid or bromate and hydrochloric acid, and the iodimetric determination of the excess of oxidizing agent. The results of analyses of a solution of hydrazine chloride agreed exactly with those obtained with the Jamieson iodic acid method. On the other hand, experiments with a mixture of bromate and sulfuric acid, in agreement with the data of Browne and Shetterly,[18] yielded low and irregular results. It is evident that the side reactions with bromic acid alone are completely or almost completely eliminated by the presence of free bromine. It seems probable that the results of the bromic acid-bromide method will be identical with the results of our bromine method in acid solution, although it is possible that there may be a compensation of small errors—a negative error due to the bromic acid side reaction, and a positive error due to the volatility of bromine.

Experiments with Bromine in Alkaline Solution.—While Browne and Shetterly found that no hydronitric acid is formed when bromine and hydrazine react in acid solution, they detected a trace of this substance in alkaline solution. An error in the analytical method was therefore possible in alkaline solution and experiments were undertaken to determine its magnitude. These experiments were performed at the same time and with the same reagents as those in acid solution.

The results were always low, that is, there was a loss of hydrazine due to side reactions. Three experiments, in which 86.71 cc. of the bromine solution was added at once to a mixture of 9.33 cc. of the hydrazine solution and 10 cc. of *N* sodium hydroxide solution (and potassium iodide and sulfuric acid added after two minutes), gave concordant results—the errors being 2.1, 2.2, and 2.3%; the final alkali concentration was calculated to be about 0.03 *N*. In a similar experiment in which the time of reaction was extended to 60 minutes, the result was almost the same, 1.9% error. In the single experiment in which the alkali concentration was increased (100 cc. of sodium hydroxide instead of 10 cc.) the error was larger, 4.1%. With a large excess of hypobromite (6.88 cc. of the hydrazine solution and 10 cc. of alkali), the percentage errors were between 2 and 3%, and no definite difference was noted when the hydrazine was added last instead of the bromine. The error observed is greater than can be accounted for by the decomposition of hydrazine in alkaline solution in the presence of air, and thus seems to be due to the simultaneous presence of hydrazine,

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[18] Ref. 1b, p. 58.

alkali, oxygen and bromine. The hypobromite method is at present useless as an accurate method for analyzing hydrazine.

The Hypochlorous Acid Method

Experimental.—The hypochlorous acid solution was prepared without difficulty by treating chlorine water with mercuric oxide in excess, distilling, and collecting the distillate.[19] It was frequently standardized iodimetrically by means of potassium iodide and dilute sulfuric acid[20] (care being taken not to make the concentrations of iodide and acid large enough to bring about the reduction of any small amount of chlorate that might be present). The solution was kept in a glass-stoppered bottle in the dark; its concentration did not decrease by more than 0.1–0.2% in 24 hours.

The hydrazine sulfate solution differed from that used in the three preceding sections. Its concentration, determined by the iodic acid method was 0.09054 *M*.

In a large number of experiments, in which hypochlorous acid in excess (usually about 20%) was added to a mixture of 9.95 cc. of the hydrazine solution, water, and 10 cc. of 6 *N* sulfuric acid, and after an interval of time the excess determined iodimetrically, the results were high (by 1 to 5%) due to the loss of chlorine gas. This gas was detected by its odor, and by its action on potassium iodide solution. Moreover, the error was decreased by increasing the dilution, which decreased the loss of chlorine. The results indicated that the reaction between hydrazine and hypochlorous acid is rapid and reproducible, and presumably quantitative except for the chlorine error.

Accordingly, a method was sought which would eliminate the error due to the volatility of chlorine. As can be seen from the equation

$$HOCl + H^+ + Cl^- = Cl_2 + H_2O \qquad (6)$$

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[19] By keeping a stream of air passing through the solution and collecting the distillate in a flask kept in a freezing mixture, there is little or no loss of hypochlorous acid during the distillation; thus when one-half of a 0.6 *N* solution of hypochlorous acid had been distilled, the distillate was approximately 1.0 *N* and the residue 0.2 *N*.

[20] The following experiments prepared by L. R. McMaster show that this method of standardization is not affected by the presence of the phosphate buffer solution (25 cc. of 0.2 *M* Na_2HPO_4 + 25 cc. of 0.2 *M* NaH_2PO_4. See Table IV). 19.88 cc. of a solution of hypochlorous acid was added to 50 cc. of the buffer solution (or of water), 20 cc. of 1% potassium iodide solution and sulfuric acid were at once added, and after about one minute the iodine was titrated with 0.0980 *N* thiosulfate.

(1) 50 cc. of water, 1 cc. of 6 *N* H_2SO_4	36.71 cc. of thiosulfate
(2) 50 cc. of buffer, 25 cc. of 6 *N* H_2SO_4	36.70 cc.
(3) 50 cc. of buffer, 10 cc. of 6 *N* H_2SO_4	36.70 cc.
(4) 50 cc. of buffer, 2 cc. of 6 *N* H_2SO_4	36.64 cc.

In another set of experiments exactly the same results were obtained when the hypochlorous acid was added to an acid solution of potassium iodide, and when the iodide and acid were added to hypochlorous acid solution.

the concentration of chlorine, and consequently its rate of vaporization, will vary directly as the concentration of hydrogen ion and chloride ion. The use of a buffer solution to maintain the concentration of hydrogen ion at a very low value proved it to be a simple method of eliminating the error due to chlorine. The buffer used was an equimolal mixture of mono- and disodium phosphates, and the concentration of hydrogen ion was thus approximately 10^{-7} N.[21]

The standard procedure recommended is as follows. Approximately 50 cc. of an equimolal mixture of mono- and disodium phosphate is introduced into a ground-glass-stoppered flask, then the hydrazine is pipetted in, and finally the hypochlorous acid added. After five minutes an excess of potassium iodide and sulfuric acid is added and the liberated iodine titrated with thiosulfate solution.

Table IV gives some of the results and the experimental conditions.

Col. 4 gives the reagent added first: H means that the hydrazine and Cl that the hypochlorous acid was added first. Col. 5 gives the time interval between the addition of the second reagent and the acidified potassium iodide, that is, the time allowed for the reaction, and Col. 6 the volume of water or buffer added to the flask before the introduction of either hypochlorous acid or hydrazine. Bf means a mixture of equal volumes of 0.2 M disodium phosphate and 0.2 M monosodium phosphate.

Table IV

The Hypochlorous Acid Method

9.95 cc. of hydrazine used in each experiment. 23.49 cc. of hypochlorous acid calcd. as 0.2 N was used in each experiment except No. 5 in which 46.98 cc. was used.

Expt.	Volume of thio. calc. as 0.1 N	Calcd. M of N_2H_4	First reagent added	Time in min.	Dilution Cc.	Diluent
1	10.93	0.0906	Cl	10	50	Bf
2	10.89	.0907	H	10	50	Bf
3	10.95	.0905	H	10	100	Bf
4	11.22	.0899	H	10[a]	100	Bf
5	57.86	.0907	Cl	10	100	Bf
6	10.88	.0907	Cl	30	50	Bf
7	10.90	.0907	Cl	5	50	Bf
8	11.03	.0903	Cl	2	50	Bf
9	9.97	.0930	Cl	5	30	0.5 N HCl
10	11.92	.0881	H	10[b]	100	Bf
11	...	.0825	H	10[c]	50	Bf

Concentration of hydrazine sulfate solution: Expts. 1, 2, 3, 5, 6, 7, 0.09065 M ± 0.2%; by iodic acid method, 0.09054 M.

[a] Waited two hours before adding the hypochlorous acid.

[b] Waited 24 hours before adding the hypochlorous acid.

[c] Waited 48 hours before determining the hydrazine by the iodic acid method. An open flask was used.

From these and other experiments, it appears that the following variations of the experimental conditions have no appreciable influence: the or-

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[21] Abbott and Bray, This Journal, **31**, 760 (1909). Washburn, *ibid.*, **30**, 36 (1908).

der of mixing the reagents, an increase in the amount of the buffer solution, the excess of the oxidizing agent, and the time above five minutes. The slightly low result in Expt. 8 indicates that two minutes is too short a time.

The high result in Expt. 9 illustrates the magnitude of the chlorine error (2.5%) when the buffer solution is replaced by dil. hydrochloric acid. This error increased with increasing acid concentration.

Expts. 4, 10 and 11 show that hydrazine decomposes slowly in the buffer solution in the presence of air, the loss being 0.9, 2.8 and 8.1% in 2, 24 and 48 hours, respectively. It is evident that this error is inappreciable when the hypochlorous acid is added at once to the hydrazine-buffer mixture. The fact that in a closed unshaken flask 0.9% of the hydrazine disappears in the first two hours, and only 1.9% in the next 22 hours, indicates that the oxygen dissolved in the solution is mainly responsible for the disappearance of the hydrazine (compare Ref. 13). The relatively high loss (8.1%) in an open flask in Expt. 11 is in agreement with this conclusion.

By averaging the six results which we have no reason to consider to be in error, the concentration of the hydrogen sulfate is found to be 0.09065 moles per liter, as against 0.09054 by the iodic acid method—a difference of only 0.12%. Our results show that the method is satisfactory,[22] provided that the hypochlorous acid solution is standardized when used, and that loss of chlorine is prevented by the use of a suitable buffer.

If this method should ever come into general use it would be worth while to replace the hypochlorous acid by a stock solution of hypochlorite in 0.25 to 0.50 *N* sodium hydroxide, since the concentration would then remain practically unchanged for a week or two. It would of course be necessary to use a more acid buffer, say monosodium phosphate or orthophosphoric acid, in amount sufficient to neutralize the alkali and to convert the hypochlorite into the acid. We have not tested this modification, but we can see no reason why it should not be accurate, since the initial solution to which the hydrazine is added can be made essentially the same as in our experiments.

Historical.—The following material is found in the literature on the chlorine-hydrazine reaction. Connick[23] in a paper on the reactions of hydrazine states: "I have carried out experiments with $N_2H_4.2HCl$, $C_6H_5.NHNH_2$ and $(CH_3)(C_6H_5)NNH_2$ with sodium hypochlorite. With all these compounds the reaction is very smooth, the nitrogen evolution

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[22] Additional evidence in favor of the accuracy of the method was obtained later by L. R. McMaster in this Laboratory. In one series of experiments 5.06 cc. of hydrazine solution was found to be equivalent to 34.81 cc. of thiosulfate solution by the iodic acid method and to 34.82 and 34.84 cc. by the hypochlorous acid method. In another independent series the average result from 6 experiments was 34.03 ± 0.04 cc. of thiosulfate solution as compared with 34.11 cc. by the iodic acid method.

[23] Connick, *Compt. rend.*, **126**, 1042 (1898).

beginning at once and continuing almost always to completion. The results are essentially the same with calcium or potassium hypochlorites." No data are given and nothing further is said.

Roberto and Roncali[24] suggest the use of hydrazine for the determination of commercial chloride of lime on the assumption that the former is oxidized to nitrogen. Their method, of which they give a detailed description, is gas-volumetric. In view of the fact, however, that in a subsequent paper[25] they make the generalization that hydrazine can be used for the quantitative determination of *all* oxygen containing oxidizing agents, specifically mentioning chlorates, peroxides, dichromates and permanganates (where we have shown that errors are unavoidable; in the case of the permanganate less than 50% of the calculated amount of permanganate being used[26]) it is evident that their results with hypochlorites could not have been accepted without further examination.

Finally Browne and Shetterly,[27] in their study of methods for the preparation of hydronitric acid, found that chlorine both in acid and alkaline solution gives "small amounts" or "traces" of hydronitric acid. In all these experiments the hydrazine was used in excess; in the experiments in acid solution the oxidizing agent was added slowly to the hydrazine and in no case was a buffer used. Since these conditions are absolutely different from those used in the hypochlorous acid method given above, and are undoubtedly favorable to the formation of ammonia and hydronitric acid, the results of Browne and Shetterly cannot be considered as evidence against our analytical method.

The Effect of Ammonia in the Above Methods

The determination of hydrazine in the presence of ammonia is of interest, not only because ammonia may be an impurity in hydrazine, but also because ammonia is formed in many reactions of hydrazine, as a by-product. Consequently, it was of interest to study the effect of ammonia on each of the above four methods.

The method adopted was to add measured amounts of ammonium sulfate solution, also of known strength, and then carry out the analysis according to the standard procedure recommended for each method. The deviation from the results obtained previously gives the magnitude of the error due to ammonia. The amount of hydrazine used was 9.97 cc. of 0.09054 M and of ammonia 14.43 cc. of 0.1099 M NH_4. The value for the concentration of ammonia was calculated from the weight of the salt dissolved.

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[24] Roberto and Roncali, *L'Industria Chimica*, **6**, 93 (1904); *Chem. Centr.*, **75**, (I) 1294 (1904).

[25] Roberto and Roncali, *L'Industria Chimica*, **6**, 178 (1904); *Chem. Centr.*, **75**, (II) 616 (1904).

[26] Compare Peterson, *Z. anorg. Chem.*, **5**, 1 (1893).

[27] Ref. 1b, p. 60.

Four runs were made with *iodic acid*, ammonium sulfate having been added in two of them. The results obtained checked within less than 0.1%, showing that the presence of ammonium salts does not interfere with this analytical method.

Similarly, four analyses made according to the *bromine method in acid solution*, ammonium sulfate having been added in two, gave identical results, showing that in this case also ammonium salts are not a source of error.

Since, as is well known, hypochlorite reacts rapidly with ammonia in alkaline or neutral solution to give nitrogen as the main product, it is evident that when ammonia is present hydrazine cannot be determined by the *hypochlorous acid method*. Similarly, ammonia as well as hydrazine would be oxidized by *bromine in alkaline solution*. Indeed, an oxidimetric method for determining ammonia by means of hypobromite has been developed,[28] and shown to be accurate when the concentration of alkali is small.

The presence of ammonium salts was found by Stollé not to interfere with his iodine method, in which sodium bicarbonate was used as a buffer. However, in the alkaline solution required in our *iodine method* the ammonia does react with iodine, and an error is introduced unless precautions are taken to avoid it.

When the excess of iodine used is small, the error is negligible. Thus, in two experiments, in which 18.8% excess of iodine and 10 cc. of *N* sodium hydroxide solution were used and the time of reaction was three minutes, the errors were only 0.15% and 0.18%; while in two similar experiments with 72% excess of iodine the errors were 7.1% and 7.9%. A black precipitate, presumably $NH_3.NI_3$, was found in the last two experiments, but not in the first two.

The error which results when a large excess of iodine is used may be decreased by decreasing the time allowed for the reaction. Thus, in two experiments with 72% excess of iodine, when the times of reaction were 0.5 and 15 minutes, the errors were 3.2% and 8.1%, respectively. In the latter case the black precipitate disappeared in about ten minutes. A comparison of the results of the four experiments with the large excess of iodine shows that the speed of the ammonia reaction decreases rapidly with time. It may indeed depend upon the amount of the nitrogen iodide precipitate, in which case the formation of nitrogen from ammonia is due to the decomposition of the solid nitrogen iodide. But, whether this is true or not, the appearance of the precipitate is evidence that the error will be appreciable.

When the nitrogen iodide precipitate is present it is undoubtedly in hydrolytic equilibrium with ammonia and hypo-iodous acid. The known

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[28] Rupp and Rössler, *Arch. Pharm.*, **243**, 104 (1905). Artmann and Skrabal, *Z. anal. Chem.*, **46**, 5 (1907).

facts that it dissolves in excess both of alkali and of acid are in agreement with this assumption; in the former case the hypo-iodous acid is removed by transformation into hypo-iodite ion, which then yields iodate and iodide; in the latter case the ammonia is converted into ammonium ion and the hypo-iodous acid into iodine when iodide is present. Accordingly, it seemed probable that the error due to ammonia would be decreased both by decreasing and by increasing the alkali concentration. This was confirmed by two more experiments with 72% excess of iodine. In one of these just enough alkali was added to discharge the iodine color; although a precipitate formed the error was only 1.0%. In the other experiment 15 cc. of 6 *N* sodium hydroxide solution was added; no precipitate formed and the error was zero.

It follows from the experiments described above that the error in the iodine method due to the presence of ammonia can be readily eliminated by the use of a small excess of iodine and a large excess of alkali.

Appendix. Other Oxidimetric Methods

The vanadic acid method proposed by Hofmann and Küspert[29] has been shown by Browne and Shetterly[1a] to yield low results on account of the formation of the by-products ammonia and hydronitric acid. When, as directed by Hofmann and Küspert, hydrazine sulfate, sulfuric acid and an excess of metavanadate solution were mixed at room temperature, and after an interval of time the mixture was heated to 60°, the volume of nitrogen evolved was found to be about 4% too small, and the result of titration with permanganate (of the vanadyl sulfate formed) about 1% too low. Browne and Shetterly proved that some hydronitric acid was formed under these conditions, and they were able to increase greatly the yield of this substance and of ammonia by adding the vanadate drop by drop to the acid hydrazine solution at 80°.

We tried a number of experiments with the oxidimetric method at the beginning of our investigation in the hope of finding experimental conditions under which the error due to side reactions was negligible or zero, but finally discontinued our work because of the unsatisfactory end-point. Series of identical experiments always showed irregular variations of ±0.5%.

The procedure usually followed was to mix the solutions at room temperature in an atmosphere of carbon dioxide, and titrate. No definite trend of the results was noted when the excess of vanadate was greatly increased, when sodium vanadate was used instead of ammonium vanadate, or when the order of mixing the reagents (at room temperature) was varied. In the last case, on the basis of the work of Browne and Shetterly, and of our own with dichromate, we believe that the results would have been low if the oxidizing agent had been added to the hydrazine solution drop by drop.

Some experiments in which the mixture was not heated showed that the reaction between hydrazine and vanadic acid is very rapid at room temperature, titration at once and after half an hour giving the same values. These results were slightly higher (less than 1%) than those obtained when the mixture was heated.

A weighted mean of all our results gave for the concentration of a hydrazine solution the same value as that obtained later by the iodic acid method. As already indicated, this check is considered to be accidental and due to a compensation of errors.

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[29] Hofmann and Küspert, *Ber.*, **31**, 64 (1898).

The Dichromate Method.—Browne and Shetterly[30] have shown that in the reaction between hydrazine and dichromate in acid solution a large amount of ammonium salt and a trace of hydronitric acid are formed when the oxidizing agent is added drop by drop. This is the condition most favorable to side reactions, and the earlier work in which quantitative oxidation to nitrogen was claimed was done under other conditions. It was thus still possible that an analytical method might be developed. However, our numerous experiments have shown that the dichromate method is useless; the results were always several per cent. in error, in the direction that too little oxidizing agent was used.

The potassium dichromate solution was standardized (1) by comparing it, through a ferrous ammonium sulfate, with the standard permanganate solution, and (2) by an iodimetric method similar to that later recommended by Vosburgh.[31] The two methods agreed within 0.1%. As in all our work the permanganate solution was standardized against sodium oxalate, and was used in determining (iodimetrically) the concentration of the thiosulfate solution.

In the experiments with hydrazine, the dichromate was always present in excess, and the time was usually about ten minutes (though in some cases it was intentionally made much larger). The excess of dichromate was then determined iodimetrically.

The reaction mixture was prepared by adding either hydrazine sulfate to a mixture of dichromate and sulfuric acid or dichromate to a mixture of hydrazine sulfate and the acid. The initial concentration of acid in the mixture was usually about 2 N. When the final reagent was added as rapidly as possible (from a calibrated pipet), the most striking feature of the first 27 experiments was the lack of reproducibility of the results. The error varied from 2 to 6%; and there was no definite evidence of a trend due to a variation in the order of mixing, the time allowed for the reaction, the temperature, or the excess of the oxidizing agent used. In a later set of experiments the error was more constant, 6 to 7%; the order of mixing, the excess of dichromate, the temperature, and the presence of a high concentration of chromic salt were found to have little or no effect; but increasing the acid concentration from 2 N to 12 N increased the error to 15.6 and 17.8% in two experiments in which the dichromate was added last.

By far the most significant factor when the acid concentration is 2 N is the rate of addition of the final reagent to the reaction mixture. The results of our experiments will be presented in a later paper.

The Fehling's Solution Method.—Browne and Shetterly[32] have shown that no hydronitric acid is formed when hydrazine is oxidized by a cupric salt in alkaline solution; and that the amount of ammonia formed, though large under some conditions, may be decreased by raising the temperature to the boiling point, by maintaining the oxidizing agent in excess at all times during the reaction, and probably by increasing the alkalinity of the solution. With Fehling's solution, under these conditions, they found that the amount of ammonia formed was negligible, and concluded that it could be used to determine hydrazine nitrometrically.

We have performed a few experiments on the corresponding oxidimetric method, with the following procedure. To about 40 cc. of a solution containing a known quantity of cupric sulfate (in excess) were added 10 cc. of a 2 M sodium potassium tartrate solution and 15 cc. of 1 N sodium hydroxide (unless otherwise stated); to this solution at a definite temperature the hydrazine solution was added; after a recorded time the mixture was acidified with sulfuric acid and the excess of cupric salt determined iodi-

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[30] Ref. 1d, p. 788; for references to earlier work see p. 785.

[31] Vosburgh, This Journal, 44, 2129 (1922).

[32] Ref. 1d, 1909, pp. 787–788. Earlier work is discussed in this paper, pp. 783–785.

metrically. The original cupric solution was standardized in the same way, and tartrate was shown not to react with iodine or iodide in neutral or acid solution.

The results were in agreement with those of Browne and Shetterly. When the reaction took place with about 60% excess of cupric salt, the result was about 5% low at room temperature, and 3% low at 90°. Lowering the concentration of alkali increased the error, while the use of 15 cc. of 12 *N* sodium hydroxide solution decreased the error to 1.8% at room temperature. With a smaller excess of cupric salt (3%) the error was increased to 11%.

It is, therefore, probable that the method would be fairly satisfactory if a strongly alkaline tartrate solution containing a large excess of cupric salt were boiled immediately before (or even during) the addition of the hydrazine solution—since the results were improved by each of the four factors: excess of cupric salt, high alkali concentration, increasing the temperature, and boiling. The boiling serves largely to eliminate oxygen of the air, and the other three factors increase the speed of the reaction between hydrazine and the cupric salt.

Summary

Four rapid and accurate volumetric methods of analysis for hydrazine have been developed, namely, iodic acid in acid solution, iodine in alkaline solution, bromine in acid solution, and hypochlorous acid in the presence of a buffer solution. These methods are practically independent of wide variations in the experimental conditions, and agree with one another within less than 0.2%.

The variation of results of these analytical methods, due to the presence of ammonium salt, was studied. The effect was undetectable in the case of iodic acid and bromine in acid solution, very large and unavoidable in the case of hypochlorous acid, and small and readily eliminated in the case of iodine.

Methods based on the use in alkaline solution of iodate and of bromine were shown to be inaccurate. The minimum error was in the neighborhood of 2%, too little oxidizing agent being used. It is suggested that this error is due to a reaction involving hydrazine, oxygen, and the second oxidizing agent (iodate or hypobromite).

Several other titration methods were investigated. The vanadate method in acid solution is unsatisfactory, though the error is not likely to be large. The dichromate method in acid solution is useless. While the error is usually large in the Fehling's solution method, it is probable that it may be made very small under the most favorable experimental conditions.

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