reported down to pressures where the observed velocity of reaction is three times the normal velocity. For electrolytic mixture of hydrogen and oxygen the α-ray effect equals the recoil-atom effect at 117mm. pressure, in a bulb 1 cm. in diameter. The departures from the calculated values at very low pressures remain to be explained.

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[CONTRIBUTION FROM THE PHARMACEUTICAL LABORATORY OF THE UNIVERSITY OF UTRECHT]

THE VOLUMETRIC ANALYSIS OF HYDRAZINE BY THE IODINE, BROMATE, IODATE AND PERMANGANATE METHODS

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Recently W. C. Bray and E. I. Cuy[1] published the results of their investigation on the quantitative titration of hydrazine. As the author also made in the past few years an investigation about the accuracy of a number of rapid oxidimetric methods for the determination of hydrazine, he thinks it a useful supplement of the communication of Bray and Cuy to describe his results.

All the substances used were purified before the stock solutions were prepared. Commercial hydrazine sulfate was recrystallized twice from water and then dried at 140°. In accordance with results of acidimetric titrations, it proved to be pure. It may be remarked here, that hydrazine sulfate is a very suitable substance to serve as a standard in acidimetric titrations. As the second dissociation constant of hydrazine is very small,[2] its salts are strongly hydrolyzed in aqueous solutions and can be accurately titrated to the basic salts with the use of methyl red as indicator: $2N_2H_4.H_2SO_4 + 2NaOH \longrightarrow (N_2H_5)_2SO_4 + Na_2SO_4 + 2H_2O$.

So with pure hydrazine sulfate one can easily determine the titer of sodium hydroxide, sodium carbonate, etc.

The potassium bromate and iodate were purified by recrystallization from water and were dried at 140°. The products obtained proved to be pure.[3] The iodine was sublimed according to the usual methods and its 0.1 N solution in 0.2 N potassium iodide was standardized against pure arsenious oxide. The potassium permanganate was a high grade commercial sample and was not further purified.

[1] Bray and Cuy, THIS JOURNAL, **46**, 858 (1924).

[2] From the results of Sommer and Weise [*Z. anorg. allgem. Chem.*, **94**, 51 (1916)] on the solubility of the hydrazine salts the approximate value for the second dissociation constant of hydrazine is calculated to be 2.8×10^{-13}.

[3] Compare Kolthoff, *Pharm. Weekbl.*, **56**, 644 (1919).

The Iodine Method

Historical.—Curtius and Schulz[4] showed that a hydrazine solution reacts with an alcoholic iodine solution according to the equation, $N_2H_4 + 2I_2 \longrightarrow N_2 + 4HI$. Stollé[5] made an application of this reaction in titrating hydrazine; he added sodium bicarbonate as a buffer. As the reaction is slow near the end-point, the last drops of iodine were added slowly, until a permanent color with starch was obtained. Rupp[6] recommended the use of Rochelle salt or sodium acetate as a buffer, addition of an excess of iodine and a back titration of this excess after 15 minutes. The method given by Stollé was applied by several authors.[7] Bray and Cuy[8] preferred a more rapid method, and added to the mixture of hydrazine solution an excess of iodine and an excess of alkali. After two minutes the solution was acidified and the excess of iodine titrated with thiosulfate solution.

Experimental.—Although the method of Bray and Cuy gave the author very good results, it is suggested that a direct titration is preferable in principle. Hence I have investigated the reaction between hydrazine sulfate and iodine under various conditions. As may be expected from the data mentioned in the literature, the rate of reaction between hydrazine and iodine depends upon the hydrogen-ion concentration of the solution: the lower the latter, the faster both substances react. In order to investigate this, 25 cc. of 0.1 *N* hydrazine sulfate solution was mixed with a buffer and titrated against 0.1 *N* iodine solution until the yellow color persisted for two minutes. The use of starch as an indicator is not advantageous, as

TABLE I

TITRATION OF 25 CC. OF 0.1 *N* HYDRAZINE SULFATE WITH 0.1 *N* IODINE

Expt.	Added buffer	P_H at end-point	Iodine taken Cc.	Error %
1	10 cc. of 2 *N* sodium acetate	5.1	24.95	−0.2
2	20 cc. of 2 *N* sodium acetate	5.4	25.03	+0.1
3	25 cc. of 2 *N* sodium acetate	5.5	25.02	+0.1
4	2 g. of Rochelle salt	5.3	25.00	0.0
5	0.5 g. of sodium bicarbonate	7.0	25.00 25.02 25.02	0.0
6	1 g. of sodium bicarbonate	7.4	25.00 25.02	0.0
7	2 g. of sodium bicarbonate	7.8	24.90 24.93	−0.4
8	2 g. of sodium bicarbonate 1 g. of cryst. sodium carbonate	9.4	24.70	−1.2
9	1 g. of sodium bicarbonate 1 g. of cryst. sodium carbonate	9.4	24.70	−1.2
10	10 cc. of 2 *N* sodium carbonate	10.1	24.45	−2.2

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[4] Curtius and Schulz, *J. prakt. Chem.*, **42,** 539 (1890).

[5] Stollé, *ibid.*, **66,** 332 (1902).

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

[7] Compare Sommer, *Z. anorg. allgem. Chem.*, **83,** 119 (1913); Oliveri-Mandalà, *Gazz. chim. ital.*, **51,** II, 201 (1921).

[8] Ref. 1, p. 863.

more time is required for the reaction with the last drops of iodine. After the end-point was reached, the Sörensen value (P_H) of the solution was colorimetrically determined.

Discussion.—Accurate results are obtained if the titration is carried out according to the method described by Stollé (Expts. 5 and 6). Care must be taken not to add too much bicarbonate (Expt. 7), for in that case insufficient iodine is taken up. As was mentioned above, the addition of starch is not advantageous, as the reaction near the end-point is then too slow. When 1 g. of sodium bicarbonate is added to 25 cc. of 0.1 N hydrazine sulfate, a good result is rapidly obtained. Only the last few drops of iodine must be added slowly; and the end-point is considered to have been reached when the yellow color persists after two minutes. Under these conditions the titration can be carried out in five to seven minutes. Good results are also obtained by the use of acetate or tartrate as a buffer (Expts. 1 to 5); but as the reaction at this higher hydrogen-ion concentration is much slower near the end-point, the addition of these substances cannot be recommended. As will be seen from Expts. 7 to 10, too low results are obtained when the P_H at the end-point is greater than about 7.5. This error is probably due to a loss of hydrazine at this low hydrogen-ion concentration.

Standard Procedure.—To 25 cc. of 0.1 N hydrazine sulfate add 0.5 to 1 g. of sodium bicarbonate and titrate with 0.1 N iodine solution, until the yellow color persists after two minutes.

The Bromate Method

Historical.—According to Browne and Shetterly[9] a solution of potassium bromate acts upon hydrazine sulfate in the presence of sulfuric acid, forming appreciable quantities of hydronitric acid and ammonia. The best yields of hydronitric acid were obtained when 5 cc. of concd. sulfuric acid was added to 100 cc. of hydrazine sulfate. These yields were calculated on the basis of the equation, $2N_2H_4 + O_2 \longrightarrow N_3H + NH_3 + 2H_2O$. The amount of hydronitric acid decreased with increasing acid concentration. Qualitative experiments showed that free bromine reacts with hydrazine sulfate without formation of hydronitric acid or ammonia. Bray and Cuy[10] using these results titrated hydrazine sulfate with a solution of bromine.

Schlötter[11] used potassium bromate in the determination of hydrazine sulfate, but the side reactions interfered in his work. Hodgkinson[12] recommends the use of copper or iron salts (in the reaction with chlorate) or molybdate as negative catalysts for the side reactions. Kurtenacker and Wagner[13] described a method on the oxidation of hydrazine with an excess of bromate and hydrochloric acid (bromide, too, may be present) and the iodimetric determination of the excess of oxidizing agent. My own results show that this method gives good results.

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[9] Browne and Shetterly, THIS JOURNAL, **30**, 53 (1908).

[10] Ref. 1, p. 865.

[11] Schlötter, *Z. anorg. allgem. Chem.*, **37**, 164, 172 (1903).

[12] Hodgkinson, *J. Soc. Chem. Ind.*, **33**, 815 (1914).

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

Experimental.—In order to obtain a rapid method for the determination of hydrazine with bromate, I have attempted to determine the conditions under which good results are obtained when the hydrazine sulfate is directly titrated with potassium bromate solution. As an indicator either methyl red or indigo was used. In the presence of an excess of bromate at the end-point, free bromine is developed, which decolorizes the indicator. As this decolorization is a time reaction, it is necessary to add the last drops of reagent slowly; thus, when the color begins to fade, a wait of one minute is recommended before the addition of the next drop. In many cases the excess of reagent was determined iodimetrically by the addition of a little potassium iodide after reaching the end-point and titration with standard thiosulfate solution. The results so obtained are recorded in Table II in the column headed "Bromate, corr."

TABLE II

TITRATION OF 25 CC. OF 0.1 N HYDRAZINE SULFATE SOLUTION WITH 0.1 N POTASSIUM BROMATE SOLUTION

Expt.	Hydrochloric acid added[a] Cc.	Initial temp. °C.	Indicator	Bromate added Cc.	Error %	Bromate corr. Cc.	Error %
1	10	100	Methyl red	23.9	−4.4	...	...
2	15	100	Methyl red	24.7	−1.2	...	...
3	10	100	Methyl red	25.05	+0.2	...	...
4	10	100	Indigo	25.07	+0.3	...	...
5	10	room	Methyl red	24.80	−0.8	24.65	−1.4
6	20	room	Methyl red	25.25	+1.0	25.02	0.0
7	20	room	Indigo	25.15	+0.6	25.03	0.0
8	25	room	Methyl red	25.22 25.24 25.23	+0.9	25.01	0.0
9	25	room	Indigo	25.14 25.15 25.12	+0.6	25.00	0.0
10	25	100	Methyl red	25.05	+0.2		
11	25		Indigo	25.03	+0.1		
12	40	room	Indigo	25.15	+0.6	25.03	+0.1
13	50	room	Indigo	25.15	+0.6	25.02	+0.1

[a] The concentration used was 4 N in Expts. 1 and 2, and 38% in all other experiments.

In order to determine whether the presence of copper and ferric salts is favorable, many experiments have been made with these salts under variable conditions. From the results it was evident that their influence was practically negligible. Molybdate also was practically without influence.

In agreement with the data of Kurtenacker and Wagner, I found that when sulfuric acid was used instead of hydrochloric acid, too low results were obtained, even when an excess of bromate was present. The special conditions (temperature) under which the method gave good results were determined, but as they are of no practical significance here, they have been omitted from this report.

Discussion.—The experiments in Table II show that concordant and reliable results are obtained in the direct titration of hydrazine sulfate with bromate when sufficient hydrochloric acid is added. In agreement with the data of Browne and Shetterly, too low results are obtained (because of side reactions) when the amount of hydrochloric acid is too small; at the beginning of the titration its concentration must be at least 20% in the solution, but increase in this concentration does not influence the result. The determination can be carried out at room temperature. With the use of indigo as an indicator, an excess of about 0.14 cc. of 0.1 *N* bromine is obtained, and with methyl red 0.22 cc. of 0.1 *N* bromine, when the liquid is decolorized. This excess can be determined iodimetrically.

Standard Procedure.—Add to the hydrazine sulfate solution the same volume of hydrochloric acid (d., 1.19) and a few drops of indigo or methyl red solution. Titrate the mixture with 0.1 *N* potassium bromate solution. When the color begins to fade, add the last drops of reagent slowly until the solution is decolorized. When indigo is used as indicator an excess of 0.14 cc. of 0.1 *N* bromate is obtained; with methyl red, the excess is 0.22 cc. at the end-point; these amounts must be subtracted as a correction. The excess can also be determined iodimetrically.

The Iodate Method

Historical.—In the presence of concd. hydrochloric acid, hydrazine reacts with iodate according to the equation, $N_2H_4 + KIO_3 + 2HCl \longrightarrow KCl + ICl + N_2 + 3H_2O$.

Jamieson[14] applied this reaction to the rapid determination of hydrazine with iodate and gave the following procedure.

"Add to 20 cc. of hydrazine salt solution 6 cc. of chloroform and 30 cc. of hydrochloric acid, and titrate with iodate until the violet color of the chloroform has disappeared." Kurtenacker and Wagner[13] confirmed the fact that this method gives correct results.

Experimental.—In my experiments 0.016 *M* potassium iodate solution was used; according to the equation, 25 cc. of 0.025 *M* hydrazine sulfate requires 37.50 cc. of this iodate solution. The experiments were carried out in ground-glass stoppered flasks; near the end-point the mixture was violently shaken, and the iodate added until the chloroform layer was decolorized. Instead of chloroform, the much cheaper carbon tetrachloride can be used with the same results. As will be seen in Table III, the concentration of the hydrochloric acid is of great importance.

TABLE III

TITRATION OF 25 CC. OF 0.025 *M* HYDRAZINE SULFATE SOLUTION WITH 0.016 *M* POTASSIUM IODATE SOLUTION

Hydrochloric acid, d., 1.19, cc.	5	10	15	20	25	40
Iodate required, cc.	39.0	37.9	37.60	37.50	37.50	37.50
Error, %	+4.0	+1.0	+0.4	0.0	0.0	0.0

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[14] Jamieson, *Am. J. Sci.*, [IV] **33**, 352 (1912).

Discussion.—As was to be expected, the concentration of the hydrochloric acid is of great importance. When its concentration is too small a positive error is obtained; when the initial acid concentration is increased to 16%, the calculated amount of iodate is absorbed. The end-point can be determined very sharply with an accuracy of 0.04 cc. of reagent.

Standard Procedure.—Add to 25 cc. of hydrazine sulfate solution in a ground-glass stoppered flask at least 25 cc. of hydrochloric acid (d., 1.19) and about 6 cc. of carbon tetrachloride, and titrate with standard iodate solution, until the carbon tetrachloride layer is decolorized after the mixture has been vigorously shaken.

The Permanganate Method

Historical.—According to Petersen,[15] hydrazine is only partly oxidized to nitrogen when it is titrated with permanganate solution at a temperature of 60° to 70° and at a sulfuric acid concentration of 10%. He gave the following equation: $17N_2H_4.H_2SO_4 + 13O \longrightarrow 13H_2O + 7\ (NH_4)_2SO_4 + 10N_2 + 10H_2SO_4$. On the other hand Roberto and Roncali[16] stated that the reaction occurs according to the normal equation, $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$. Medri[17] tried to explain the discrepancy between these reports and stated that the oxidation is more complete with decreasing acid concentration. Neither he nor Browne and Shetterly[18] succeeded in clearing up this question. Sabanajeff[19] concluded from his results that alkaline permanganate can completely oxidize the hydrazine to nitrogen.

Experimental.—Our potassium permanganate solution was freshly prepared before the experiments were made, and was standardized against pure oxalic acid and sodium oxalate (Sörensen).

In the first experiments the direct titration (without the use of an excess of permanganate) of hydrazine sulfate was applied. As the reaction occurs at room temperature very slowly, the mixture of hydrazine sulfate and acid was boiled and then titrated with permanganate solution.

When sulfuric acid was used as acidifying agent, the liquid was pink after the addition of a few cubic centimeters of permanganate and the color disappeared slowly. In order to increase the rate of reaction, I boiled the solution again and added more reagent, until the pink color was permanent. This titration therefore was not very convenient.

When hydrochloric acid was used as acidifying agent, quite different results were obtained; the mixture of hydrazine sulfate and hydrochloric acid was boiled and then was directly titrated, until the end-point was reached; thereafter the pink color disappeared slowly.

The results are recorded in Table IV.

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[15] Petersen, *Z. anorg. allgem. Chem.*, **5,** 1 (1893).

[16] Roberto and Roncali, *Ind. chim.*, **6,** 178 (1904). Compare *Chem. Zentr.*, **1904,** II, 616.

[17] Medri, *Gazz. chim. ital.*, **36,** II, 373 (1906).

[18] Browne and Shetterly, THIS JOURNAL, **31,** 221 (1909).

[19] Sabanajeff, *Z. anorg. allgem. Chem.*, **20,** 21 (1899).

TABLE IV

DIRECT TITRATION OF 25 CC. OF 0.1 *N* HYDRAZINE SULFATE WITH 0.1 *N* PERMANGANATE SOLUTION

	Sulfuric acid				Hydrochloric acid			
Expt.	1	2	3	4	5	6	7	8
Acid added, 4 *N*, cc.	5	10	20	30	5	10	20	30
Permanganate required, cc.	19.5	19.5	19.6	19.55	25.00	25.03	25.05	25.10

In order to determine the effect of an excess of permanganate, other experiments were made under various conditions.

A mixture was prepared of 20 cc. of 0.1 *N* hydrazine sulfate with the amount of acid, bicarbonate or sodium hydroxide given in Table V, and 50 cc. of 0.1 *N* permanganate solution. After the time indicated in the table, the excess of permanganate was iodimetrically titrated back in acid solution. From the data obtained, the amount of permanganate reduced by the hydrazine was calculated; this quantity is also shown in the table.

TABLE V

OXIDATION OF 20 CC. OF 0.1 *N* HYDRAZINE SULFATE WITH 50 CC. OF 0.1 *N* PERMANGANATE SOLUTION

Expt.	Substance added	Time before back-titration H.	M.	Permanganate required Cc.
9	5 cc. of 4 *N* H_2SO_4		30	9.2
10	5 cc. of 4 *N* H_2SO_4	24		9.2
11	10 cc. of 4 *N* H_2SO_4		30	9.2
12	25 cc. of 4 *N* H_2SO_4	24		9.3
13	25 cc. of 4 *N* H_2SO_4		30	9.4
14	25 cc. of 4 *N* H_2SO_4	24		9.8
15	2 g. of $NaHCO_3$		30	19.7 19.8
16	2 g. of $NaHCO_3$	24		19.6 19.8
17	5 cc. of 0.4 *N* NaOH		30	20.03
18	5 cc. of .4 *N* NaOH	24		20.05
19	10 cc. of .4 *N* NaOH		30	20.04
20	10 cc. of .4 *N* NaOH	24		20.05

Discussion.—When we consider at first the results obtained in the direct titration with permanganate (Table IV), we see that the oxidation occurs in sulfuric acid medium at boiling temperature in the ratio of 5 molecules of hydrazine to 4 molecules of oxygen; we have not investigated the nature of the products formed under these conditions. This titration cannot be recommended for analytical purposes.

In hydrochloric acid the reaction occurs according to the normal equation: $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$. By means of this reaction the strength of a hydrazine solution may rapidly be determined. A variation of the acid concentration over a wide range proved to have no effect (Expts. 5 to 8). When an excess of permanganate is used the oxidation in acid solution is far from complete; 20 molecules of hydrazine require about 9 molecules of oxygen.

In agreement with the results of Sabanajeff[19] we found that in alkaline solution the hydrazine is completely oxidized by the permanganate, and on this we can base the following simple and rapid method for the determination of hydrazine.

Standard Procedures.—A. *In Acid Solution, Direct Titration:* To 25 cc. of 0.1 *N* hydrazine sulfate solution add 10 cc. of 4 *N* hydrochloric acid, heat the mixture to the boiling point and titrate with 0.1 *N* permanganate solution until the liquid is pink. This color disappears after a short time.

B. *In Alkaline Solution, Indirect Titration:* To 20 cc. of 0.1 *N* hydrazine sulfate add 50 cc. of 0.1 *N* permanganate solution and 10 cc. of 4 *N* sodium hydroxide. After half an hour add 1.5 g. of potassium iodide and 20 cc. of 4 *N* sulfuric acid, and titrate the liberated iodine with 0.1 *N* thiosulfate solution.

In both cases the hydrazine is completely oxidized according to the equation: $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$.

Summary

1. The determination of hydrazine with iodine according to Stollé gives rapid and accurate results when less than 1 g. of sodium bicarbonate to 25 cc. of 0.1 *N* hydrazine sulfate is added. The use of starch as an indicator cannot be recommended. The rate of reaction between iodine and hydrazine decreases with increasing hydrogen-ion concentration.

2. Hydrazine can be directly titrated with bromate, when sufficient hydrochloric acid is added. Indigo or methyl red may be used as indicator. When the concentration of the acid is less than required, side reactions occur.[9]

3. The iodate method of Jamieson[14] gives accurate results when a sufficient amount of hydrochloric acid is present.

4. Hydrazine can be directly titrated with permanganate in the presence of hydrochloric acid. The determination must be started at the boiling point.

5. Hydrazine is also completely oxidized by alkaline permanganate solution. This reaction is the basis for a rapid and accurate method for its determination.

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