

Cc. of Sample Taken	Conc. Sulfuric Acid Used Cc.	Found Cc.	Error Per cent
1.94	20	9.98	9.71
1.94	20	9.98	9.8
10	15	51.4	51.3
10	Slightly acidified	51.4	49.9
10		51.4	50.5

Certain of the above-measured gas volumes were passed into caustic and showed practically complete absorption. In addition, a 25-cc. portion of the bicarbonate solution was evacuated without acidifying. A reading of 1.7 cc. was obtained, equivalent to a blank of 0.068 cc. of gas per 1 cc. of sample or slightly less than 1.4 per cent of error. When, however, we consider that a part of this blank was undoubtedly due to a decomposition of the bicarbonate under very greatly reduced pressure the error approaches the vanishing point. In this connection, 25 cc. of ordinary distilled water were acidified and evacuated and a reading of less than 0.4 cc. found. This represents 0.3 per cent error, as compared with 1.4 per cent.

Another check was run upon the method by passing carbon dioxide through approximately 0.05 *N* sulfuric acid. This 0.05 *N* acid represented the approximate free mineral acidity of some of the mine water with which the author was working and was used as another standard solution.

The carbon dioxide was determined by the modified nitrometer method and by the titrimetric method (phenolphthal-

ein cold—phenolphthalein hot) using 0.1 *N* sodium hydroxide. The sample was allowed to stand in the laboratory in a large, poorly stoppered bottle for 6 hrs., and again analyzed by both methods.

Table II shows the results obtained:

	Carbon Dioxide P. p. m.
10:00 A. M. Titration Gasometric	402 422 <sup>1</sup>
4:00 P. M. Titration Gasometric	354 381 <sup>1</sup>

<sup>1</sup> Caustic absorption practically complete.

Since the prevailing tendency of the gasometric method is, under these conditions, low, the above figures, while hardly conclusive, indicate that the growing opinion against phenolphthalein as an indicator in carbon dioxide titrations is well founded. Numerous other determinations were made which gave logical, consistent figures.

It is believed that the apparatus as outlined can be conveniently adapted to field work. It was not found necessary to assemble the apparatus for this purpose, but the matter has been given some consideration for possible future use. There appear to be no difficulties that cannot be readily overcome. Care will be taken to standardize properly the dimensions of the apparatus.

## The Effect of the Presence of Filter Paper on Permanganate-Oxalate Titrations<sup>1</sup>

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In the analysis of limestone, lime, and cement, the determination of calcium is most rapidly made by titrating a hot acid solution of the precipitated calcium oxalate with permanganate. To insure complete solution of the oxalate from the filter paper, many analysts find it most convenient to add the paper itself to the solution and to allow it to remain suspended in the liquid during the titration. Indeed, the American Society for Testing Materials<sup>2</sup> has adopted such a procedure as a tentative method for analyzing limestone and lime although in the method as given, the greater part of the calcium oxalate is washed from the filter paper with hot water and the paper containing the remainder of the oxalate<sup>3</sup> is added to the solution near the end of the titration. Several textbooks give essentially the same procedure.<sup>4</sup> The fact that permanganate may be reduced by filter paper shreds is generally known, and Myhill<sup>5</sup> has recently emphasized this point in connection with permanganate titrations. For this reason, Gooch<sup>6</sup> filters the calcium oxalate upon asbestos, and others<sup>7</sup> dissolve from the filter paper by means of prolonged washing with hot, dilute sulfuric acid. The extent of this reduction under the conditions of ordinary volumetric titrations is not given, however, and whether or not the effect is great enough to affect appreciably the accuracy of ordinary analytical results is not generally known.

### EXPERIMENTAL DETAILS

In the following experiments 0.1 *N* solutions of oxalic acid and potassium permanganate were used, and all titra-

<sup>1</sup> Received July 5, 1921.

<sup>2</sup> *Proc. Am. Soc. Testing Materials*, 20 (1920), 632.

<sup>3</sup> Hot water will not remove all the calcium oxalate from the paper. See U. S. Geological Survey, *Bulletin* 700, 147.

<sup>4</sup> Low, "Technical Methods of Ore Analysis;" Cheever-Smith, "Select Methods in Quantitative Analysis."

<sup>5</sup> *Chem. Age (London)*, 4 (1921), 151.

<sup>6</sup> Gooch, "Methods in Chemical Analysis."

<sup>7</sup> Sutton, "Volumetric Analysis;" Treadwell-Hall, "Analytical Chemistry," II.

tions were made by means of weighing burets. The ratio of permanganate to oxalic acid was repeatedly established during each series of experiments, and in all determinations the end-point was taken as a faint pink remaining permanent for at least 15 sec. The filter papers were Baker and Adamson's 9-cm. washed papers weighing approximately 0.45 g. each. Since the extent of disintegration and hence the reducing power of the filter paper could not be accurately controlled, it could hardly be expected that the results obtained under apparently similar conditions would be in perfect agreement, but the values obtained checked closely enough to give a fairly accurate idea of the extent of reduction in each case.

The first and second series of titrations were carried out with the object of determining under varying conditions of time and concentration the extent of reduction of an excess of permanganate when kept in contact with filter paper. In the first series, 60 drops (4.6 cc.) of 0.1 *N* KMnO<sub>4</sub> were added from a weighing buret to 350 cc. of water containing 20 cc. of 6 *N* H<sub>2</sub>SO<sub>4</sub> and heated to 70° C. A filter paper was submerged in the solution and allowed to remain for a

TABLE I—REDUCTION OF 0.1 *N* POTASSIUM PERMANGANATE BY FILTER PAPER, VARYING TIME OF CONTACT

Vol. KMnO<sub>4</sub> = 4.6 cc. Vol. soln. = 350 cc. Conc. KMnO<sub>4</sub> = 0.042 g./l.

Time of Contact Min.	Total Vol. H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> Cc.	Total Vol. KMnO <sub>4</sub> Cc.	KMnO <sub>4</sub> Equivalent to H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> <sup>1</sup> Cc.	Vol. 0.1 <i>N</i> KMnO <sub>4</sub> Reduced Cc.
1	4.38	4.71	4.57	0.14
1	4.59	4.95	4.79	0.16
1	4.40	4.78	4.60	0.16
3	4.23	4.67	4.42	0.25
3	4.37	4.79	4.56	0.23
3	4.57	5.02	4.77	0.25
7	4.20	4.72	4.38	0.34
7	4.10	4.62	4.28	0.34
7	4.18	4.73	4.37	0.36
20	4.06	4.75	4.24	0.51
20	4.20	4.86	4.38	0.48
20	4.48	5.19	4.68	0.51

<sup>1</sup> Ratio = 1.044.

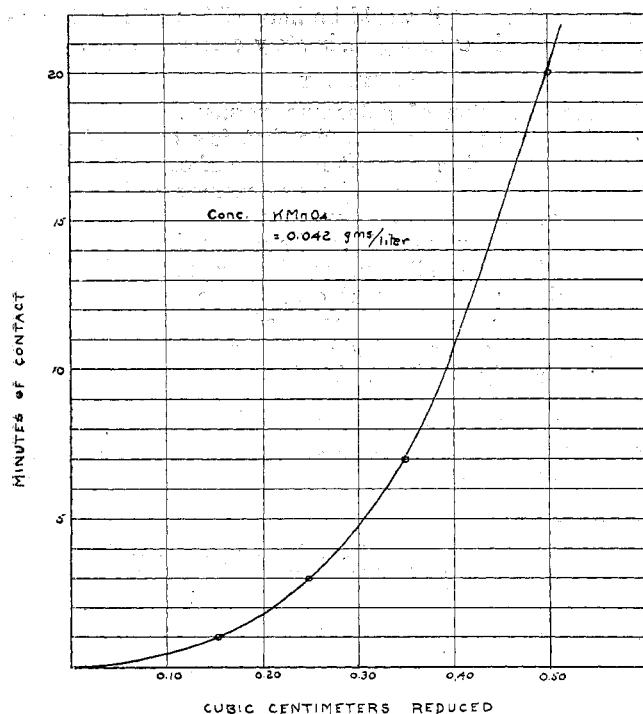


FIG. 1—GRAPH SHOWING REDUCTION OF POTASSIUM PERMANGANATE BY CONTACT WITH FILTER PAPER UNDER CONDITIONS GIVEN IN TABLE I. RESULTS IN TERMS OF 0.1 N  $\text{KMnO}_4$ .

specified length of time, during which the solution was occasionally stirred and the paper allowed to disintegrate only of its own accord. An excess of the standard oxalic acid was quickly added and the titration was finished with the permanganate. The volume of permanganate used up by the filter paper was calculated in each case in terms of 0.1 N  $\text{KMnO}_4$ , and the values obtained are given in Table I. Similar titrations were made keeping the time of contact with the filter paper constant and varying the concentration of the excess permanganate. The numerical results of this series in terms of 0.1 N  $\text{KMnO}_4$  are given in Table II. Figs.

TABLE II—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER, VARYING CONCENTRATION OF EXCESS PERMANGANATE

Time of Contact = 3 Min.						
Vol. $\text{KMnO}_4$ Cc.	Vol. Soln. Cc.	Conc. $\text{KMnO}_4$ G./L.	Total Vol. $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Total Vol. $\text{KMnO}_4$ Cc.	Vol. $\text{KMnO}_4$ Equivalent to $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Vol. 0.1 N $\text{KMnO}_4$ Reduced Cc.
0.24	350	0.0022	0.49	0.62	0.51	0.11
0.24	350	0.0022	0.20	0.32	0.21	0.11
0.24	350	0.0022	0.26	0.38	0.27	0.11
0.77	350	0.0070	0.92	1.11	0.96	0.15
0.77	350	0.0070	0.76	0.95	0.79	0.16
0.77	350	0.0070	0.77	0.96	0.81	0.15
1.9	350	0.017	1.75	2.03	1.83	0.20
1.9	350	0.017	1.72	2.02	1.80	0.22
1.9	350	0.017	2.20	2.48	2.29	0.19
4.6	350	0.042	4.23	4.67	4.42	0.25
4.6	350	0.042	4.37	4.79	4.56	0.23
4.6	350	0.042	4.57	5.02	4.77	0.25
4.6	125	0.110	4.26	4.74	4.44	0.30
4.6	125	0.110	5.24	5.78	5.47	0.31
4.6	125	0.110	4.19	4.67	4.38	0.29

<sup>1</sup> Ratio = 1.044.

1 and 2 show in graphic form the averages of the results given in Tables I and II. From these graphs it is seen that the reduction of permanganate by filter paper increases very rapidly with the first few drops of excess permanganate and in the first few moments of contact—facts which in themselves show the danger of titrating with permanganate in the presence of filter paper.

In the third series of titrations, 200 cc. of water containing 20 cc. of 6 N  $\text{H}_2\text{SO}_4$  were heated to 70° C., standard oxalic acid was added from a weighing buret, a filter paper was

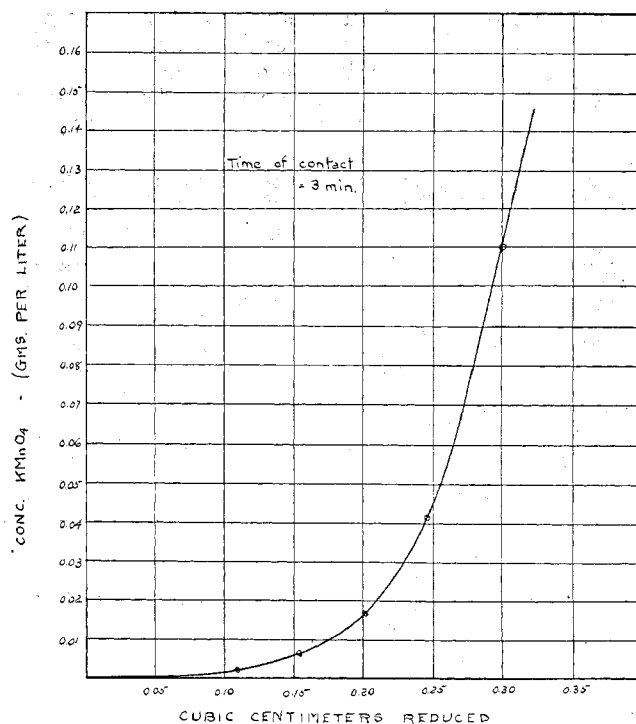


FIG. 2—GRAPH SHOWING REDUCTION OF POTASSIUM PERMANGANATE BY CONTACT WITH FILTER PAPER UNDER CONDITIONS GIVEN IN TABLE II. RESULTS IN TERMS OF 0.1 N  $\text{KMnO}_4$ .

submerged in the liquid, and the solution was titrated with the standard permanganate. In each titration the permanganate was added slowly, allowing the solution to become decolorized between each drop, and the filter paper was broken up as little as possible. The results given in Table III show that, under the given conditions, the average volume of 0.1 N  $\text{KMnO}_4$  reduced by the filter paper is about 0.03 cc.

TABLE III—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATION

Vol. $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Vol. $\text{KMnO}_4$ Cc.	Vol. $\text{KMnO}_4$ Equivalent to $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Vol. 0.1 N $\text{KMnO}_4$ Reduced Cc.
2.674	2.786	2.758	0.028
2.082	2.176	2.148	0.028
2.569	2.674	2.651	0.028
2.566	2.689	2.647	0.042
2.674	2.790	2.759	0.031
1.979	2.078	2.043	0.035
3.211	3.338	3.313	0.025
4.024	4.176	4.152	0.024

Av. 0.030

<sup>1</sup> Ratio = 1.032.

As in all permanganate-oxalate titrations, with the first few drops of permanganate the resulting solution is decolorized only very slowly, during which time the permanganate may be very appreciably reduced by any filter paper shreds present. This source of error may be reduced either by adding a few cubic centimeters of manganous sulfate solution previous to the titration, or by adding the filter paper shortly before the completion of the titration as mentioned above. The effect of the previous addition of manganous sulfate is shown in Table IV, and the effect of adding the filter paper late in the titration is shown in Table V where, incidentally,

TABLE IV—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATIONS, ADDING MANGANOUS SULFATE

Vol. $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Vol. $\text{KMnO}_4$ Cc.	Vol. $\text{KMnO}_4$ Equivalent to $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Vol. 0.1 N $\text{KMnO}_4$ Reduced Cc.
2.057	2.132	2.122	0.010
3.131	3.249	3.220	0.020
3.628	3.754	3.744	0.010
3.306	3.432	3.411	0.021
3.478	3.605	3.588	0.017
5.225	5.414	5.392	0.022

<sup>1</sup> Ratio = 1.032.

Av. 0.017

the total volume of  $\text{KMnO}_4$  used is more nearly comparable to the volume used in an average limestone or cement analysis. In each case the average reduction of permanganate is decreased by about 50 per cent, or to a point where the error is hardly greater than the error involved in reading an ordinary buret.

TABLE V—REDUCTION OF 0.1 N POTASSIUM PERMANGANATE BY FILTER PAPER IN DIRECT OXALATE TITRATIONS, ADDING FILTER PAPER WITHIN ABOUT 2 Cc. OF THE END-POINT

Vol. $\text{H}_2\text{C}_2\text{O}_4$ Cc.	Vol. $\text{KMnO}_4$ Cc.	Vol. $\text{KMnO}_4$ Equivalent to $\text{H}_2\text{C}_2\text{O}_4$ <sup>1</sup> Cc.	Vol. 0.1 N $\text{KMnO}_4$ Reduced Cc.
18.675	19.120	19.105	0.015
26.264	26.892	26.868	0.024
20.716	21.203	21.193	0.010
11.914	12.203	12.188	0.015
43.990	45.014	45.002	0.012
			Av. 0.015

<sup>1</sup> Ratio = 1.023.

Similar titrations in the presence of filter paper which had been thoroughly disintegrated gave such fugitive end-points, and were accompanied by such considerable reductions of

permanganate, that it would be impossible under such conditions to obtain even approximately correct results.

#### SUMMARY

1—The reduction of potassium permanganate by filter paper increases rapidly with the first few drops of excess permanganate and in the first moments of contact.

2—In titrating oxalates with permanganate in the presence of filter paper, except in cases where great accuracy is required, satisfactory results may be obtained either by previously adding a small amount of manganous sulfate and titrating slowly, taking great care not to disintegrate the paper; or better by washing most of the oxalate from the paper with hot water and adding the paper only when the titration is nearly complete. In either case, the error caused by the presence of the filter paper is hardly greater than the error involved in the reading of an ordinary buret.

3—Satisfactory results cannot be obtained in any case where the filter paper is present in highly disintegrated form.

## The Formation of Oxides of Nitrogen in the Slow Combustion and Explosion Methods in Gas Analyses<sup>1,2,3</sup>

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### INTRODUCTION

As a part of its investigation pertaining to a more efficient utilization of the natural resources of the country and greater safety in mining methods, the Bureau of Mines has occasion to make many analyses of gases from mines. These gases vary from samples of mine air taken under good ventilation conditions to those from mine fires and gases after explosion disasters and the like.

The accuracy of analysis is important, and constant endeavor is made to develop better methods and refinements in gas analysis.

This report deals with the production of oxides of nitrogen when gases are analyzed by the slow combustion and explosion methods under the usual conditions of analysis.

### PURPOSE OF INVESTIGATION

The question relative to the production of oxides of nitrogen when combustible gases are burned by slow combustion using a glowing platinum spiral, or by explosion using an electric spark, has been much discussed by authorities on gas analyses.

White<sup>4</sup> finds that large errors result when combustible gases are burned by the slow combustion method and attributes these errors to oxides of nitrogen, since tests made with Greiss's reagent give positive results, and concludes that the slow combustion method is unreliable for accurate gas analysis. Dennis,<sup>5</sup> on the other hand, finds that, "when the spiral was heated for 5 min. to a temperature of dull redness in 100 cc. of air, the colorimetric determination of the nitrite that was formed showed that the amount of the oxides of nitrogen produced did not in any case exceed 0.005 cc. and that the volume is usually much less than this." Dennis further states that under the most unusual conditions the volume of oxides of nitrogen formed was less than 0.01 cc., which in technical gas analysis is inappreciable.

<sup>1</sup> Received August 3, 1921.

<sup>2</sup> Presented before the Division of Industrial and Engineering Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

<sup>3</sup> Published by permission of Director, U. S. Bureau of Mines.

<sup>4</sup> "The Oxidation of Nitrogen as a Source of Error in the Estimation of Hydrogen and Methane," *J. Am. Chem. Soc.*, **23** (1901), 476.

<sup>5</sup> "Gas Analysis," 1913, 152.

The greater part of the routine analytical work in gas analysis at the Pittsburgh Experiment Station of the U. S. Bureau of Mines consists in the analysis of samples of gases from metal and coal mines. The percentages of total combustibles in these samples are very low, in most cases less than 0.2 of one per cent. For this work gas apparatus of the Haldane type as modified by Burrell<sup>1</sup> is used.

Haldane apparatus is so constructed that volumes can be read to an accuracy of about 0.002 cc. It has a limit of accuracy of about 0.02 per cent when the three combustible gases, methane, carbon monoxide, and hydrogen, are present.

In this method the combustibles are burned with a platinum spiral heated to a bright yellow. It is evident that if appreciable amounts of oxides of nitrogen are formed this method cannot be used since contractions would be produced even when combustibles were absent. When normal air is passed into the slow combustion pipet and the spiral heated to a bright yellow for 3 min., the contraction produced seldom exceeds 0.005 cc. and in most cases is found to be less than 0.002 cc.

To prove or disprove whether these small contractions were due to oxides of nitrogen, ten different platinum wires of No. 28 B & S gage were investigated under conditions as used in analysis.

The wires, 2.25 in. long and wound into a spiral as used in gas analysis, were heated for different periods of time, and at different temperatures, and the resulting gases analyzed for oxides of nitrogen by the method to be described. The greater number of the tests were made with normal air containing no combustible since this condition more nearly approximates the condition in actual use.

### OXIDES OF NITROGEN BY THE SLOW COMBUSTION METHOD

The procedure of making the tests was essentially as follows: The platinum wire to be tested having been assembled in the combustion pipet of the Haldane apparatus, about 20 cc. of laboratory air were drawn into the buret and accurately measured, then passed into the KOH pipet and the carbon dioxide removed. The gas volume was again read, passed into the combustion pipet, and burned for a determined

<sup>1</sup> G. A. Burrell and F. M. Seibert, U. S. Bureau of Mines, *Bulletin* **42**, "The Sampling and Analyses of Mine Gases and Natural Gas."