

## Oxides of Nitrogen in Ozonized Air

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There is very little agreement among the numerous papers which have been published on the content of oxides of nitrogen in ozonized air. The divergence in results might be attributed to either the method of analysis or the performance of the individual ozone generator. There are many methods for the determination of nitric acid and the oxides of nitrogen but the common method for analysis of ozone involves the reaction between potassium iodide and a measured volume of ozonized oxygen. The iodine liberated by the ozone is determined by the standard thiosulfate method. The method of analysis has been criticized on the basis that oxides of nitrogen which are present in ozonized air also liberate iodine.

However, it has been established that nitric oxide and nitrogen dioxide do not exist as such in the presence of ozone but are oxidized to nitric anhydride (1, 2). Furthermore, it has been established by many investigators (3, 4, 5, 6) that pure, dilute nitric acid is not an oxidizing agent.

As much as 75 per cent of the oxidizing material in ozonized air is claimed by Thorpe (7) to be oxides of nitrogen. No method of analysis is given but in a later publication (8) the same author mentioned the use of diphenylbenzidine (9) as a colorimetric method for the determination of nitric acid. Ewell (10) has stated that only traces of nitric anhydride are present in ozonized air. In a recent publication, Watson (11) reported two laboratory type ozone generators which produced only 1 part of nitric anhydride to 2,580 and 30,150\* parts of ozone, respectively. Gorodetzki (12) has reported the formation of about 2 per cent of nitric anhydride in ozonized air. Briner and Papazian (13) found that commercial oxygen containing about 2.2 per cent nitrogen gave only a trace of nitric anhydride when ozonized. Calculated as nitric oxide, it amounted to about 0.00014 per cent of the volume of oxygen. The method of analysis consisted of the absorption of the nitric anhydride in a given volume of ozonized oxygen by means of dilute aqueous alkali, reduction of the nitrate to nitrite by zinc and the latter substance determined colorimetrically by the Griess-Ilosvay method.

The usefulness of ozonized air and the action of ozone on oxides of nitrogen as a method for fixation of nitrogen has been investigated (14, 15, 16) and found not feasible.

The most feasible method for the estimation of nitric anhydride seemed to be as nitric acid. The determination of nitric acid as nitron nitrate (17) has been established as a reliable method (18, 19). Schultz and Wulf (15), and Watson (11) have shown complete absorption of

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\* The value may have been a typographical error.

nitric anhydride in water and dilute aqueous alkali. However, the fog which is produced when ozonized air is bubbled into aqueous solutions has been shown by Anderegg and McEachron (20) to consist of nitric acid. Collection of a known volume of ozonized air and analysis of it for nitric acid would obviate the error which might occur from incomplete absorption if the gas was bubbled through water or aqueous alkali.

The ozone generator consisted of three Berthollet tubes connected in series. The apparatus was modeled after the ozone generator described by Smith (21) but with certain modifications (22).

### Procedure

Ozonized air was swept through a dry 3-liter flask for two hours, then the stopcocks turned so as to by-pass the flask. Fifty ml. of 0.1 N sodium hydroxide solution was added to the flask by means of a dropping funnel which was attached to the flask by means of a ground glass joint. The flask was removed, capped and the solution agitated frequently. The solution was allowed to stand over night in the flask to insure complete absorption of the nitric anhydride vapor.

The contents of the flask were poured into a 500-ml. Erlenmeyer flask and the inside of the 3-liter flask washed with three 25-ml. portions of distilled water. The alkaline solution was heated at its boiling point for a few minutes to destroy the ozone. The hot solution was acidified with 5 ml. of glacial acetic acid and then 10 ml. of nitron acetate solution containing 0.33 g. of nitron was added. The solution was allowed to cool to room temperature and as the nitron nitrate crystals began to form, it was agitated frequently. The solution was placed in a refrigerator over night. The temperature in the refrigerator remained consistently at  $8 \pm 1^\circ$  C. The nitron nitrate was collected in a weighed Gooch crucible and dried to constant weight at  $85\text{--}90^\circ$  C. A correction was made for the solubility of nitron nitrate (23).

The volume of ozonized air was corrected to standard conditions and the percentage of nitric anhydride calculated from the weight of nitron nitrate.

### Discussion

Nitric oxide and nitrogen dioxide are not completely absorbed in either an alkaline solution or in water and the aqueous solution will give a test for nitrite. To determine whether or not nitrous acid was formed, ozonized air was bubbled through water and the latter substance tested for nitrite. The presence of nitrous acid could not be detected when the sulfanilic acid alpha-naphthylamine test (24) was used. To further ascertain that the method of absorption was not at fault, an analysis was made in which the nitric anhydride was absorbed in dilute sulfuric acid containing hydrogen peroxide (25); the methods checked one another satisfactorily. It was also necessary to determine whether or not there was an accumulation of nitric anhydride in the flask. To do this, ozonized air was passed through the flask for six hours then the gaseous contents of the flask analysed for nitric anhydride. No accumula-

tion of nitric anhydride had occurred since the percentage was the same as in previous trials.

The effect of voltage and the rate of flow of air was studied. The data and results are given in Table I.

Table I

Det'n #	Rate l/hr.	Voltage, M.	Vol. of	Nitron Nitrate, g.	Per cent N <sub>2</sub> O <sub>5</sub>	
			ozonized air, cor., ml.		Vol.	Wt.
1	22	10	3010	0.1393	0.142	0.530
2	22	10	3105	0.1434	0.134	0.500
3	22	12	3012	0.1818	0.180	0.671
4	22	10	3053	0.1412	0.139	0.518
5	22	8	3022	0.1019	0.101	0.376
6	22	6	2971	0.0462	0.046	0.172
7	18	10	3042	0.1723	0.169	0.630
8	15	10	3089	0.1958	0.190	0.708

As shown in Table I, at 10,000 volts and a rate of 22 liters per hour the nitric anhydride in the ozonized air averaged about 0.52 per cent by weight. The amount was increased at 12,000 volts and was reduced to 0.17 per cent at 6,000 volts. A decrease in the rate of flow of the air resulted in an increase in the percentage of nitric anhydride. This effect of the rate of flow has been observed by Schultz and Wulf (15).

A series of determinations were made to ascertain the effect of nitric anhydride on the sodium thiosulfate titration. Ozonized air was bubbled through a 5 per cent potassium iodide solution at a rate of 8.9 liters per hour for three-minute intervals and the iodine determined by the usual method, using 0.1161 molar sodium thiosulfate solution. The apparatus was arranged so that the ozonized air could be either passed through a trap cooled with a mixture of ether and solid carbon dioxide or by-passed directly to the potassium iodide solution. The temperature of the cooling bath was  $-68^{\circ}$  C. Much of the nitric anhydride was removed by the freezing process since only a small amount of fog was formed above the potassium iodide solution and its accumulation was also visible in the trap. The volume of the sodium thiosulfate solution used for each determination is shown in Table II.

Table II

Det'n #	Thiosulfate ml.	Det'n #	Thiosulfate ml.	Det'n #	Thiosulfate ml.
1	8.45	5	8.73	9	8.75
2	8.60	6	8.76	10	8.73
3	8.73	7	8.77	11	8.63
4	8.53	8	8.50		

In determinations 1,2,6,7,10 and 11 the ozonized air was not passed through trap. The average of these values is 8.66 ml. The average of the determinations in which ozonized air was passed through the trap cooled to  $-68^{\circ}$  C. was 8.65 ml. This would indicate that at lower concentrations of nitric anhydride in ozonized air, it does not interfere with the determination of ozone when the potassium iodide method is used.

To accumulate considerable nitric anhydride, ozonized air was passed through the cooled trap for approximately 1.5 hours, then the trap was by-passed and the cooling bath removed. After the trap had warmed in the air for about five minutes, the stream of ozonized air was directed through it at the same rate as used previously. The nitric anhydride was removed in about four minutes but the ozonized air was allowed to continue to pass for exactly five minutes. It required 16.88 ml. of the sodium thiosulfate solution for titration of the iodine which had been liberated from the potassium iodide. On the basis of the previous results, it should have required 14.42 ml. of the sodium thiosulfate solution; this would indicate that a high concentration of nitric anhydride does interfere with the determination of ozone.

Operating at 10,000 volts, the ozonized air from the ozone generator contained 2-3 per cent ozone by volume, depending upon the rate of flow of air.

### Summary

1. The concentration of nitric anhydride in ozonized air was determined by hydrolysis of the anhydride to nitric acid which was determined by the nitron method.
2. The amount of nitric anhydride in ozonized air is dependent on the voltage and rate of flow of air.
3. The nitric anhydride in ozonized air does not interfere with the determination of ozone by the potassium iodide sodium thiosulfate method.

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