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# Continuous Determination of Nitric Oxide and Nitrogen Dioxide in the Atmosphere

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Continuous determinations of nitric oxide and nitrogen dioxide in the atmospheric air by the use of a modified Saltzman reagent will be described. Measurement was made intermittently, once every 30 min., by an automatic continuous analyzer equipped with a single-path colorimeter. The response of the analyzer was obtained as an average of the concentration of nitrogen oxides over a period of 25 min. Two bubblers were used for absorbing nitrogen oxides into the modified Saltzman reagent, whose transmittance was measured for the determination. One bubbler was designed to absorb nitrogen dioxide, and the other, nitric oxide plus nitrogen dioxide after the oxidation of the nitric oxide by permanganate. The oxidizing efficiency of the permanganate was 96—100 per cent. The acetic acid in the Saltzman reagent was replaced with *n*-propyl alcohol in the modified Saltzman reagent; the spontaneous coloration and corrosive quality of the reagent was decreased by this substitution. The concentration of nitric oxide was obtained from the difference between the two responses of the analyzer, while the concentration of nitrogen dioxide could be read directly from the indication of the recorder. The transmittance ratio method was applied to the measurements, accurate determinations were possible, even at high blank values. Therefore, the reagent was used repeatedly by cycling it on the basis of measuring the difference in the coloration of the reagent before and after the absorption of nitrogen oxides. The analyzer could be used for a long period without changing the reagent.

The maximum allowable concentration and the warning concentration of nitrogen dioxide are 5 p. p. m. and 0.5 p. p. m. respectively,1) but those of nitric oxide are not known in the present stage of our knowledge. As these oxides are interchangeable under atmospheric conditions, the determination of nitric oxide should be made together with that of nitrogen dioxide for purposes of air-pollution control.

Some apparatuses for the determination of nitrogen dioxide have been designed by several researchers.2,3) Among these Thomas and his coworkers developed a continuous-determination apparatus for both nitrogen oxides provided with a triple-path colorimeter.4) A continuous analyzer for nitrogen oxides equipped a single-path colorimeter will be described in this paper.

This analyzer determines the amoung of nitrogen oxides once every 30 min. by integrating them in the liquid absorber, whose transimittance is measured for the determination of the nitrogen oxides. A transmittance ratio method developed by Hisky5) and by Bastian6) was applied to the analyzer accurate measurements were then possible, even at high values of the blank. The absorber can be repeatedly used in the system, and the differences in the transmittances of the liquid, before and after the absorption of the gases, indicate the average concentrations of the nitrogen oxides during the period being considered.

Nitrogen dioxide gives color to the color-developing reagent, which is simultaneously the absorber of the gas, and nitric oxide reacts with the reagent after being oxidized to nitrogen dioxide by a sulfuric acid solution of potassium permanganate. Saltzman reagent was modified and successfully used for this purpose.

## Reagents

**The Modified Saltzman Reagent.**—The absorbing and color-developing reagent: Disslove100

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1) *Am. Ind. Hyg. Assoc. J.*, **23**, 419 (1962).

2) F. E. Adley and C. P. Skillerm, ibid., **19**, 233 (1958).

3) S. Yanagisaws, S. Mitsuzawa, A. Hirose and M. Arai, *Japan Analyst (Bunseki Kagaku)*, **12**, 1937 (1963).

4) M. D. Thomas and J. A. Macleod, *Anal. Chem.*, **28**, 1810 (1956).

5) C. F. Hisky, ibid., **21**, 1440 (1949).

6) R. Bastian, ibid., **22**, 160 (1950).

g. of sulfanilic acid, 1 g. of *N*-(1-naphthyl)-ethylenediamin dihydrochloride, and 200 ml. of *n*-propyl alcohol (or *s*-butyl alcohol) into distilled water, and then make up the volume to 20 l.

**Standard Solution.**—Dissolve 0.154 g. of sodium nitrite, which has been dried at 105—110°C for 3 hr., into distilled water, and make up the volume to 1 l.; then dilute 10 ml. of this solution to 1 l. Each milliliter of the solution thus prepared is equivalent to 0.001 ml. of nitrogen dioxide gas in the standard state (0°C, 760 mmHg).

**Oxidizing Solution.**—Dissolve 25 g. of potassium permanganate in 500 ml. of a 2.5% solution of sulfuric acid.

## The Modification of Saltzman Reagent

Saltzman reagent[7] is prepared by dissolving 100 g. of sulfanilic acid, 1 g. of *N*-(1-naphthyl)-ethylenediamine dihydrochloride and 100 ml. of acetic acid into distilled water, and making up the volume to 20 l. This reagent is colored spontaneously over a long period; this color interferes with the measurement of the absorbance of the reagent-$NO_2$ complex. This reagent also corrosively attacks the metallic and plastic parts of the analyzer. Thus, acetic acid was eliminated from the reagent in order to avoid the corrosion of the apparatus. On the other hand, 200 ml. of *n*-propyl alcohol (or *s*-butyl alcohol) was tentatively added to lower the surface tension of the reagent and to increase its gas-collection efficiency, for the reason that the acetic acid was added to Saltzman reagent was to minimize the surface tension of the reagent. Moreover, the acetic acid in Saltzman reagent lowers the pH of the solution. However, it was found that the pH of the solution was sufficiently low even if acetic acid was omitted, as it was 1.5.

The changes in the spontaneous coloring with the time of Saltzman reagent and the modified reagent are shown in Table I. It is believed that the discoloration is accelerated by the light and the temperature. In view of this, the reagent solution tanks in the equipment were all made dark boxes.

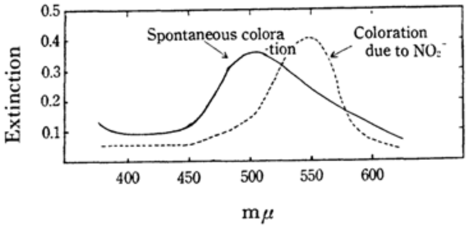

Fig. 1. Spontaneous coloring of Saltzman reagent.

Saltzman reagent and the modified reagent take, respectively, 12 min. and 15 min. to reach a full color development at 20°C. The gradient of the working curve resulting from the modified reagent was 10.6 % lower than that from Saltzman reagent.

## Oxidation of Nitric Oxide

The reagent is colored by a coupling reaction with nitrogen dioxide, but not by nitric oxide, so nitric oxide must be oxidized before the reaction with the reagent.

There have previously been established three ways to oxidize nitric oxide; gas-phase oxidation, by a solid catalyzer, and liquid-phase oxidation. It is known that the oxygen-oxidation or air-oxidation method is effective in oxidizing nitric oxide

TABLE I. CHANGE IN SPONTANEOUS COLORING WITH TIME OF THE ABSORBING AND COLOR DEVELOPING REAGENT

(Reference: distilled water, 540 mμ, 20 mm.-cell, Transmittance—%)

| Storage container, 500 ml. | No. of days | | | | |
|---|---|---|---|---|---|
| | 0 | 3 | 10 | 20 | 30 |
| SALTZMAN'S REAGENT | | | | | |
| White polyethylene bottle | 99.7 | 94.3 | 85.5 | 80.2 | 76.3 |
| Brown polyethylene bottle | 99.7 | 95.8 | 89.0 | 86.0 | 84.0 |
| Brown polyethylene bottle (in refrigarator) | 99.7 | 79.5 | 94.0 | 93.5 | 91.3 |
| White polyethylene bottle (25°C) | 99.7 | 87.0 | 81.6 | 75.4 | 72.0 |
| MODIFIED REAGENT | | | | | |
| White polyethylene bottle | 99.7 | 99.5 | 99.0 | 98.3 | 97.2 |
| Brown polyethylene bottle | 99.7 | 99.7 | 99.4 | 99.0 | 98.0 |
| White polyethylene bottle (25°C) | 99.7 | 96.7 | 93.4 | 90.0 | 86.0 |

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7) B. E. Saltzman, *Anal. Chem.*, **32**, 135 (1960).

of a higher concentration,[8] but the reaction takes place very slowly for nitric oxide of a lower concentration, such as one in atmospheric air; this method of oxidation, therefore, is not applicable to the continuous determination of nitric oxide in atmospheric air.[9] Thomas reported that an ozone concentration of 0.3 p. p. m. was suitable for oxidizing the air sample in his continuous analyzer,[4] but it is not easy to keep the concentration of ozone constant, and, furthermore, ozone decomposes the reagent sometimes it even oxidizes the atmospheric nitrogen. Therefore, the ozone-oxidation method was not used in this research.

Silica gel and active carbon are often used as oxidizing agents of nitric oxide,[10] but they are not preferably used because they are effective only for nitric oxide of a higher concentration, and also because they absorb nitrogen dioxide. Among the liquid-phase oxidizing agents, potassium permanganate in a sulfuric acid solution, potassium bichromate in a sulfuric acid solution, and hydrogen peroxide in a sulfuric acid solution, etc., 2.5% of potassium permanganate dissolved in 2.5% sulfuric acid has been used by several researchers for the oxidation of nitric oxide with Saltzman reagent.[11,12]

The oxidizing agant is placed in a vessel made of glass, and the air sample is bubbled through a ball filter of fritted glass (G-1), 30 mm. in outside diamater.

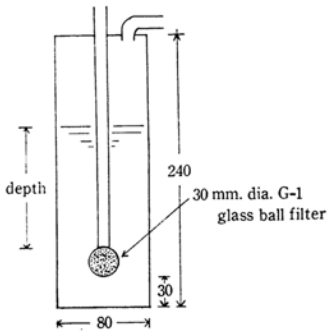

Fig. 2. The oxidation vessel.

The relation between the oxidizing efficiency and the depth of the oxidizing liquid is shown in Table II.

TABLE II. THE RELATION BETWEEN THE DEPTH OF THE OXIDIZING LIQUID AND THE OXIDIZING EFFICIENCY

| Depth of liquid cm. | Volume of liquid ml. | Oxidizing efficiency<br>2.5% $KMnO_4$-2.5% $H_2SO_4$ solution | <br>2.5% $KMnO_4$-15% $H_2SO_4$ solution |
|---|---|---|---|
| 5 | 270 | 96% | 100% |
| 9 | 560 | 100% | 100% |
| 15 | 840 | 100% | 100% |

In these experiments 2.7 p. p. m. of nitric oxide in nitrogen was passed through at a rate of 150 ml./min. for 5 min. As is shown in Table II, the oxidizing efficiency is higher at higher concentrations of sulfuric acid, at which concentrations the oxidizing reagent decomposes itself over a long period. 2.5% sulfuric acid was used for the practical oxidation by placing a glass tube with a ball filter of fritted glass deeper than 10 cm. below the surface of the oxidizing liquid, through this tube the air sample was dispersed into the liquid.

## Apparatus

A schematic diagram of the gas and liquid flow system is show in Fig. 3, while the program of the operation of the analyzer is shown in Table III. The valves ($V_1$—$V_5$) are operated for the periods indicated in Table III; the analysis operation advances toward the right with the passage of time, and the solenoid valves, the timer, the piston pump and the programmer motor are actuated in the framed parts.

The gas-absorbing bubbler is shown in Fig. 4. The air sample is introduced into the absorbing bubbler, which contains 50 ml. of the reagent,

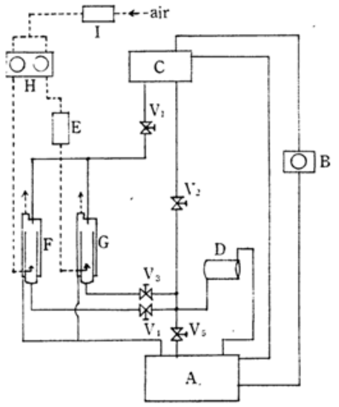

Fig. 3. Diagram of gas and liquid flow system in the nitric oxide - nitrogen dioxide analyzer. $V_1$—$V_5$, solenoid valves; A, solution tank (20 l.); B, solution pump; C, head tank; D, cell; E, oxidation vessel; F, $NO_2$ bubbler; G, $NO+NO_2$ bubbler; H, air pump; I, dust filter

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[8] S. W. Nicksic and J. Harkins, ibid., **34**, 985 (1962).

[9] O. Tada, *J. of Science of Labour (Rodo Kagaku)*, **40**, 185 (1964).

[10] T. Kiba, "Shokubai Kagaku Gairon" (Outline of Catalytic Chemistry), Kyoritsu Shuppan, Tokyo (1956), p. 212.

[11] M. B. Jacobs, "The Chemical Analysis of Air Pollutants," Interscience Publishers, New York (1960), p. 215.

[12] Second Subcommittee. Japan Society of Air Pollution, "Taikiosen no Sokutei" (Determination of Air Pollutants), Corona Sha, Tokyo (1962), p. 159.

TABLE III. ANALYSIS PROGRAM

| Analysis operations | Measure reaction solution | Introduce sample air | Fill cell | Zero point check | Liquid discharge | Fill cell | $NO+NO_2$ determ. | Liquid discharge | Fill cell | $NO_2$ determ. | Liquid discharge |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Time, min. | 0.5 | 25 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Programer moter | ROTATE | — | ROTATE | | | | | | | | |
| Timer | — | ROTATE | — | — | — | — | — | — | — | — | — |
| Solution valves | | | | | | | | | | | |
| $V_1$ | OPEN | — | — | — | — | — | — | — | — | — | — |
| $V_2$ | — | — | OPEN | — | — | — | — | — | — | — | — |
| $V_3$ | — | — | — | — | — | OPEN | | | — | — | — |
| $V_4$ | — | — | — | — | — | — | — | — | OPEN | | |
| $V_5$ | — | — | — | — | OPEN | — | — | OPEN | — | — | OPEN |
| Gas pump | GAS SUCTION | | | — | — | — | — | — | — | — | — |

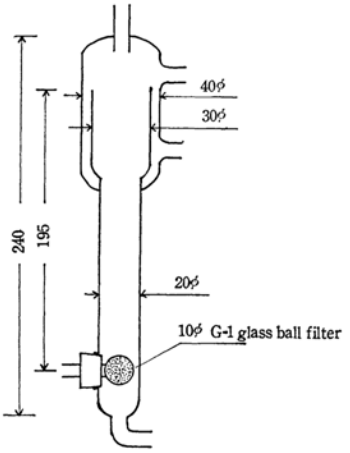

Fig. 4. The absorbing bubbler.

the volume being measured by an over-flow system. The absorbing efficiency of this bubbler by gas sample was 96—98% under the actual conditions of analysis.

The air sample is divided into two parts, one is led into the first bubbler directly, while the other is led through the oxidizing liquid to the second bubbler. The air sample is bubbled for 25 min. at a constant rate of 150 ml./min. by means of a piston pump. The nitrogen dioxide in the air sample is integrated during a 25 min. period in the first bubbler, and both nitric oxide and nitrogen dioxide, in the second bubbler. Then, the transmittances of the reagents for the determinations of nitrogen oxides are measured in a colorimetric cell in the order of the reagent blank, the reagent colored by nitrogen dioxide, and that colored by both nitrogen dioxide and nitric oxide. The ratios of the transmittances of the working reagents, which show the concentrations of nitrogen dioxide and of nitric oxide plus nitrogen dioxide, are plotted on the recorder in a logarithmic scale as the averages of 25-min. measurements. The concentration of nitric oxide is obtained by subtracting the concentration of nitrogen dioxide from that of the sum of nitric oxide and nitrogen dioxide.

Thomas used the reagent repeatedly by treating it with active carbon,[4] but generally the reagent used for the continuous determination is discarded without re-processing.[2,3] In this experiment, the reagent was not re-processed and used repeatedly, and the reagent blank was determined in each determination, for the re-processing system was considered not very reproducible and it might make the apparatus rather complicated. Correct determinations can be made in the range of the linear part of the calibration curve, even if the reagent itself is colored; therefore, a transmittance-ratio method[5,6] was applied to the analyzer, and accurate measurements were possible even at higher values of the blank. The larger volume of the reagent reservoir could be helpful for a long-run determination. The reagent was replaced when it reached a definite absorbance, as was determined by monitoring by an absolute transmittance meter.

The electric circuit is shown in Fig. 5.

In the first step, the blank reagent is led into the colorimetric cell, and the switch, S, is connected to (1); at this stage a voltage corresponding to a

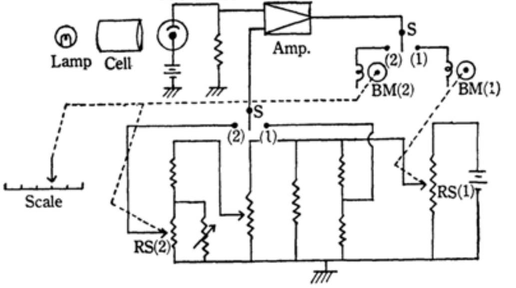

Fig. 5. Diagram of instrument circuit.

photo-current appears at both ends of the sliding resistance, RS(2), as a result of automatical balancing by RS(1). Then, the reagent colored is led to the cell; a voltage corresponding to the photo-current in this stage is represented by the position of the contact point of the sliding resistance when the switch, S, is connected to (2). The transmittance ratio of two optical measurements are represented by the voltages in this stage of the resistances. Then, each transmittance ratio of the reagents, that of nitrogen dioxide to the blank and that of nitrogen dioxide plus nitric oxide to the blank, is plotted on the recorder separately, and the indications are read out in a logarithmic scale graduated from 0 to 5 p. p. m.

## Examples

Three of these analyzers are used at the National Institute of Hygienic Science, Tokyo.

Analytical data on nitrogen dioxide and nitric oxide collected at the Continuous Air-monitoring Station of the Institute, Kasumigaseki, Tokyo, from January through December, 1964, are shown in Table IV. An example of the determination is shown in Fig. 6, in which the average concentrations of the nitrogen oxides during the period from January to March, 1964, is graphically displayed, along with the time of day. The avarage concetration of nitric oxide was several times that of nitrogen dioxide; it seems that these results were intensely affected by pollution from the automobiles near the Monitoring Station.

This analyzer has played an improtant role in monitoring air pollution and in analyzing the mechanism of that pollution in Japan.

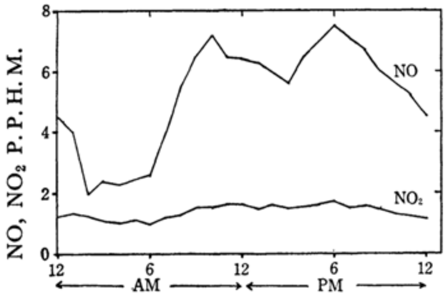

Fig. 6. An example of analysis of the atmospheric air.

TABLE IV. ANALYTICAL DATA OF NITROGEN DIOXIDE AND NITRIC OXIDE IN TOKYO
(Continuous air monitoring station at Kasumigaseki, Tokyo)

Nitrogen dioxide (p. p. h. m.)

| Date | Number of determination | Each determination | | Hour-average | | Day-average | | Average | Standard deviation |
|---|---|---|---|---|---|---|---|---|---|
| | | min. | max. | min. | max. | min. | max. | | |
| 1964. 1 | 685 | 0.5 | 4.0 | 0.9 | 1.5 | 0.4 | 2.4 | 1.3 | 0.62 |
| 2 | 605 | 0.5 | 5.0 | 1.0 | 1.6 | 1.0 | 1.9 | 1.3 | 0.56 |
| 3 | 520 | 0.5 | 3.5 | 1.2 | 1.8 | 1.0 | 2.2 | 1.5 | 0.53 |
| 4 | 650 | 0.5 | 4.0 | 1.8 | 2.4 | 1.6 | 2.5 | 2.1 | 0.64 |
| 5 | 612 | 0.5 | 4.0 | 1.5 | 2.2 | 1.6 | 3.0 | 2.0 | 0.33 |
| 6 | 622 | 0.5 | 4.0 | 1.6 | 2.4 | 1.8 | 2.6 | 2.0 | 0.61 |
| 7 | 657 | 0.5 | 5.0 | 1.8 | 2.4 | 2.0 | 2.4 | 2.1 | 0.13 |
| 9 | 586 | 0.5 | 5.0 | 1.7 | 2.6 | 2.0 | 2.5 | 2.2 | 0.72 |
| 10 | 638 | 1.0 | 5.0 | 1.8 | 2.4 | 2.0 | 2.6 | 2.2 | 0.29 |
| 11 | 648 | 1.0 | 6.0 | 1.9 | 3.0 | 2.0 | 3.2 | 2.3 | 0.82 |
| 12 | 616 | 1.0 | 5.0 | 2.0 | 2.7 | 1.9 | 3.2 | 2.4 | 0.64 |

Nitric oxide (p. p. h. m.)

| Date | Each determination | | Hour-average | | Day-average | | Average | Standard deviation |
|---|---|---|---|---|---|---|---|---|
| | min. | max. | min. | max. | min. | max. | | |
| 1964. 1 | 0.5 | 32.0 | 2.2 | 9.7 | 2.6 | 10.5 | 6.7 | 4.93 |
| 2 | 0.5 | 21.0 | 1.2 | 6.6 | 0.7 | 9.8 | 4.1 | 3.91 |
| 3 | 1.0 | 30.0 | 2.0 | 6.8 | 2.3 | 10.8 | 4.8 | 3.37 |
| 4 | 1.0 | 15.0 | 1.9 | 5.5 | 2.5 | 9.8 | 4.2 | 2.41 |
| 5 | 0.5 | 15.0 | 1.9 | 4.5 | 1.0 | 9.7 | 3.2 | 2.76 |
| 6 | 0.5 | 6.0 | 0.9 | 2.5 | 0.8 | 3.3 | 1.8 | 1.25 |
| 7 | 1.0 | 8.0 | 1.2 | 3.3 | 1.1 | 4.7 | 2.4 | 1.52 |
| 9 | 0.5 | 21.0 | 1.3 | 7.5 | 1.0 | 10.6 | 4.9 | 4.44 |
| 10 | 1.0 | 24.0 | 1.3 | 9.2 | 2.6 | 9.6 | 5.6 | 4.01 |
| 11 | 1.0 | 21.0 | 1.4 | 7.2 | 1.8 | 9.9 | 4.5 | 3.54 |
| 12 | 1.0 | 51.0 | 1.5 | 13.3 | 2.2 | 15.1 | 7.2 | 6.27 |

## Conclusions

Saltzman reagent has been modified and acetic acid has been replaced with *n*-propyl alcohol (or *s*-butyl alcohol) as a surface-active agent, decreases in the spontaneous coloration and in the corrosive quality of the reagent have resulted, and better results of the determination have been obtained in the continuous analysis.

The intermittent measurement system of the continuous analyzer has made the apparatus simpler, and the data obtained are convenient for statistical data processing.

The re-cycling of the reagent has made it possible to run a continuous determination for a long time, even for more than a month in the winter time.