Measurement of Ambient Nitrogen Oxides over an Extended Period of Time by Means of a Solid Absorber Technique

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(Received October 27, 1978)

A new technique using a solid substance for the absorption of nitrogen oxides in the atmosphere was developed in order to obtain an average concentration of nitrogen oxides over a period of several weeks. Nitrogen oxides is absorbed by an absorbent (alkaline earth metal peroxide), and the nitrate produced in the absorber is extracted into water to determine the amount of nitrate by the ion-selective electrode method. The concentration of atmospheric nitrogen oxides is calculated from the amount of nitrate in the extract. A quantitative relation was found between the amount of nitrogen oxides collected on the absorber and that of nitrate in the extract. Hydrogen peroxide produced by the reaction of the absorber and water did not interfere with the measurement of nitrate by the ion-selective electrode technique. Practicability of this technique was demonstrated in comparison with the automatic recording analyzer (NO_x meter) with the Saltzman reagent.

Liquid absorber techniques using absorption bottles and impingers are the most popular and convenient for analysis of gaseous pollutants in the atmosphere.[1,2] These methods are suitable for obtaining hourly or short term concentrations of air pollutants. However, they require a tedious averaging process for weekly or monthly averages. A filter paper impregnated with some reagents can also be used for sampling gaseous pollutants, such as fluorides, sulfur dioxide and nitrogen dioxide, but no report seems to have apeared on the measurement of nitrogen oxides by this method. Cuddeback *et al.*[3] reported on the use of copper shot for the collection of nitrogen dioxide, but the sampling time of this method is 24 h or less. Measurement of average concentration over a long duration of time is often necessary for practical purposes such as the biological evaluation of air pollution and studies of the corrosion of metals.

In this investigation, we attempted to develop a technique to obtain an average concentration of nitrogen oxides over a period of several weeks, using a solid substance for the absorption of nitrogen oxides in the atmosphere. Peroxides of alkaline earth metals were chosen as absorbents since (1) they absorb nitrogen dioxide and (2) they oxidize the nitrogen oxide to dioxide in the presence of humidity and the resulting nitrogen dioxide is absorbed. The nitrate produced in the absorber is extracted into water for determination of the amount of nitrate by the ion-selective electrode method. The concentration of nitrogen oxides in the air can be calculated from the concentration of nitrate.

Experiments were carried out to study the possible interference by hydrogen peroxide in the determination of nitrate, to determine the capacity of the peroxide agents in the absorption of nitrogen oxides, and to examine relevant parameters. Among the peroxides of alkaline earth metals, barium peroxide was found to be the most suitable, and was rested over a period of two weeks. The practicability of this technique was demonstrated in comparison with the automatic recording analyzer (NO_x meter) with the Saltzman reagent.

Experimental

Apparatus and Reagents. Ion-selective electrode for nitrate: Type 93-07 (Orion Co.) electrode was used and the electrode potential was measured with a pH-mV meter (Type M-5, Hitachi-Horiba Co.) against a reference electrode, type 90-02 (Orion Co.), which has a double-junction reference electrode filled with the Orion filling solution (Cat. No. 90-00-02) in the inner chamber. The response of the (pH-mV) meter was recorded on a QPD-54 recorder (Hitachi Co.).

Absorbents for nitrogen oxides: Magnesium peroxide (Kyowa-Kagaku Co.) and commercial calcium peroxide, strontium peroxide and barium peroxide of the first grade were used. They were formed into tablets of $3\phi \times 5$ mm.

Autoanalyzer of nitrogen oxides: Type GP-5B, Denki-Kagaku-Keiki Co. using the Saltzman reagent.

Calibration Curve. The calibration curve of nitrate concentration was made with potassium nitrate (1—100 ppm). Calibration curves were prepared for each absorbent (MgO_2, CaO_2, or SrO_2) by dissolving 5 g of each in water and then adding a fixed amount of nitrate to the solution followed by dilution to 50 ml with water. A series of standard solutions thus prepared were passed through a filter paper to remove the peroxide and oxide from the solution, and the nitrate and a small amount of hydroxide of alkaline earth metals produced in the absorbent during the sampling were filtered off. 2 ml of 2M-$(NH_4)_2SO_4$ and 1 ml of 1M-H_3BO_3 were then added to the filtrate in order to adjust the ionic strength and to keep the stability of the nitrate in the measurement by an ion-selective electrode.[4] For the standard solution with barium peroxide, a procedure to remove the barium ions was necessary before the addition of $(NH_4)_2SO_4$ and H_3BO_3. For this purpose, excess 2M-$(NH_4)_2SO_4$ (2 ml) was added to the solution and the resulting $BaSO_4$ was filtered off. The volume of the solution was then made to 50 ml by adding water, with the addition of 1M-H_3BO_3 for the measurement of nitrate.

Capability Tests of Absorbents. The 1 ppm nitrogen dioxide gas was prepared by the nitrogen dioxide permeation tube technique with clean air, and the 1 ppm nitrogen oxide was prepared by the dilution of 50 ppm nitrogen oxide from the tank with clean air. Concentrations of these gases were measured with an automatic recording spectrometer using the Saltzman reagent. The amount of absorption of nitrogen oxide and nitrogen dioxide was determined by the difference in concentrations of these gases in the air flow before and after exposure to the absorbents, and the amount was compared with that of nitrate measured by the ion-selective electrode technique.

Results and Discussion

Calibration Curve. The calibration curves of nitrate for each absorbent are shown in Fig. 1. The

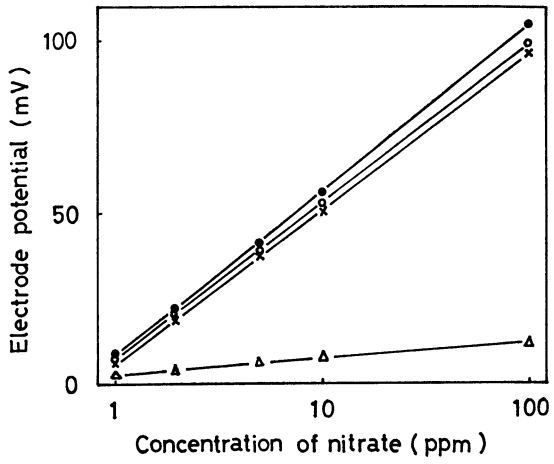

Fig. 1. Calibration curve of nitrate with each absorbent.
●: BaO_2, ○: CaO_2, ×: MgO_2, △: SrO_2.

sensitivity of nitrate measurement varies with peroxide, the order of sensitivity being $BaO_2 > CaO_2 > MgO_2 > SrO_2$. BaO_2, CaO_2, MgO_2 can be used, but BaO_2 was chosen for practical use because of its longer life as compared to that of the other peroxides.

Effect of Hydrogen Peroxide on the Nitrate Measurement by Ion-selective Electrode. Hydrogen peroxide is produced by dissolving the alkaline earth metal peroxides in water in a reaction as follows.

$$MO_2 + 2H_2O = M(OH)_2 + H_2O_2$$

where M denotes the atom of alkaline earth metal. The possible interference of hydrogen peroxide on the nitrate solutions of 10 and 100 ppm was examined by the addition of 30% hydrogen peroxide. The electrode potential generated by nitrate ions was not affected by hydrogen peroxide in the range 0.001—0.1%. This indicates that the influence of hydrogen peroxide is negligible in a solution containing 10—20 ppm of hydrogen peroxide. Kuroda endorsed this by an experiment in which he used a hydrogen peroxide solution containing phosphoric acid in the sampling of nitrogen oxides in the analysis of gaseous industrial effluents.[5] He reported that the presence of hydrogen chloride and sulfur dioxide does not interfere with analysis of nitrogen oxides. No examination of the interferences was carried out.

Absorption of Nitrogen Oxides by Barium Peroxide. The time variation of the absorption efficiency of nitrogen oxides to barium peroxide is shown in Fig. 2. Nitrogen oxide and dioxide each of concentration 1 ppm and 5 g of barium peroxide were used. The absorption efficiency of nitrogen dioxide did not change throughout 40 h, but that of nitrogen oxide decreased slightly with time, being higher than 90% after 40 h. The decrease of absorption might be attributed to a decrease in the power of the peroxide to oxidize the nitrogen oxide to dioxide.

It has been shown that 50 g of barium peroxide can remove more than 90% of nitrogen oxide from the air one month under sampling conditions of flow rate 300 ml/min and relative humidity<40%.[6] The absorption capacity of barium peroxide was demonstrated by the

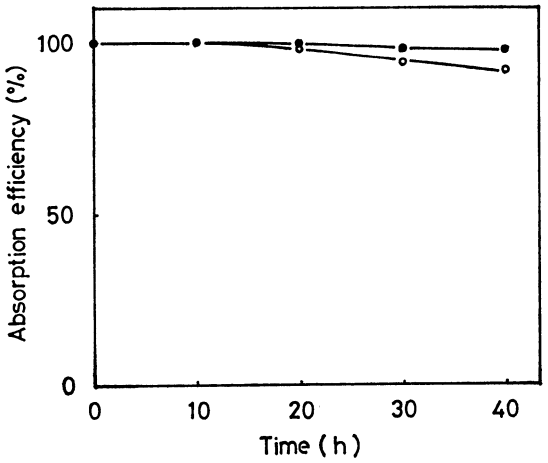

Fig. 2. Change in absorption efficiency of barium peroxide with time.
Weight of absorbent: 5 g, temperature: 25 °C, relative humidity: 50%, flow rate of gas: 300 ml/min.
Concentration of nitrogen oxide and dioxide: 1 ppm each.
●: NO_2, ○: NO.

removal of nitrogen oxides from the air at the air inlet of an automatic NO_x meter; 50 g of barium peroxide showed complete removal of nitrogen oxides of background levels for two weeks. If an alkaline layer is placed before the peroxide layer, the former absorbs only nitrogen dioxide and the latter only nitrogen oxide. This could be utilized in a simultaneous measurement of nitrogen oxide and dioxide.

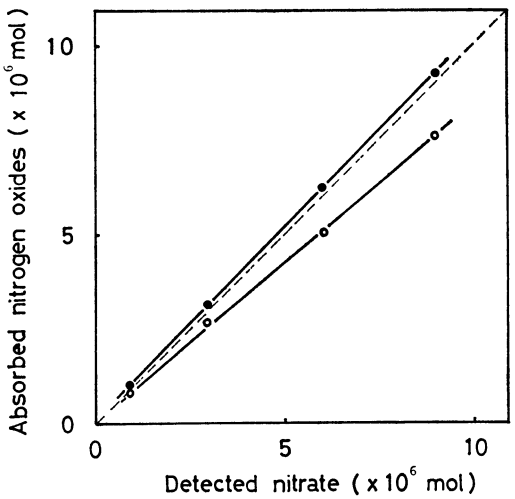

Fig. 3. Comparison of the amounts of absorbed nitrogen oxides and detected nitrate.
●: NO_2, ○: NO.
(Dotted line shows an ideal equivalent line.)

Relations between the amount of nitrogen oxides measured by NO_x meter and that of nitrate measured by the ion-selective electrode are shown in Fig. 3, where the amount of nitrate is 20% higher than that of nitrogen dioxide. The difference might be caused by the lower estimation of nitrogen oxide by the NO_x meter resulting

from the low oxidation efficiency of the $KMnO_4$–H_2SO_4 solution. If the low efficiency (80%) is corrected, the ratios of the amount of absorbed nitrogen oxides to the amount of nitrate measured by use of the peroxide become almost 1 both for nitrogen oxide and dioxide (Fig. 3). The amount of nitrogen oxides was controlled by changing the absorption time, keeping the concentration of nitrogen oxides constant.

Table 1. Comparison of data obtained by the solid sampling technique and by NO_x according to the conventional method

Date	From '78 Jan. 1st till '78 Jan. 14th		From '78 Jan. 15th till '78 Jan. 28th	
Analytical method	Solid absorbent method	Auto-analyzer	Solid absorbent method	Auto-analyzer
Concentration of NO_x in the atmosphere	0.061	0.048	0.052	0.045

Comparison of the Present Method with an Automatic NO_x *Meter.* Tests of our technique were made by setting up the barium peroxide samplers and an automatic recording analyzer for nitrogen oxides by absorption spectrometry with the Saltzman reagent for field measurements. These apparatus were operated together for two weeks, and data obtained from them were compared. Average concentrations of nitrogen oxide and dioxide during two weeks were calculated from the hourly values by the NO_x meter. The peroxide absorbent was pulverized in a mortar; 5.0 g out of the 50 g absorber was treated by the same procedure as that for the preparation of the calibration curve. The average concentrations during this period, in the first half and the latter half of January in 1978, were 0.061 and 0.052 ppm by the present method, and 0.048 and 0.045 ppm by the NO_x meter. If corrections owing to the low conversion efficiency of nitrogen oxide to dioxide were made on the latter, the data by NO_x meter would be 0.054 and 0.051. Real comparison would not be made in this way, but the concentrations obtained by the present technique are close to those by the NO_x meter. Advantages of the solid absorber technique are: (1) the size of sampling device is small, convenient for transport, (2) preparation and handling of the sampling tube is simple, (3) adjustment of the flow rate is simpler than that in the bubbling system, the shape and grain size of the peroxide being unchanged throughout the sampling period.

Conclusion

In a long run measurement, the average concentration of the nitrogen oxides can be obtained by a simple technique using a solid absorber of barium peroxide. The measurement was made by means of nitrate determination in the peroxide absorber by the use of an ion-selective electrode technique. Since the sensitivity of the ion-selective electrode, which requires 50 ml of an aliquot, is 1 ppm for the solution to be measured, the practical sensitivity of this technique for nitrogen oxides determination is 10^{-6} mol. No special cases or adjustments were required in two weeks sampling. The values of concentration of nitrogen oxides in the atmosphere were very close to those found by the NO_x meter. Advantages of this solid absorber technique are simplicity in operation and stability of air flow rate in sampling.

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