DETERMINATION OF AMBIENT CONCENTRATION OF NO BY CHEMILUMINESCENCE AND ELIMINATION OF TRACE IMPURITY NOx IN DILUENT GAS USED FOR CALIBRATION

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Introduction

Recently, NO_x detection systems utilizing the principal chemiluminescent reaction between NO and O_3 have been developed and commercially available[1-4]. However, these are the systems applied largely to mobile source measurements at high concentrations of ppm level.

In the present work, we designed a NO and NO_x detection system to monitor ambient concentration of ppb level. According to our design, this was tentatively constructed by Yanagimoto Co., Ltd.. Because of the known quenching effect of air on the $NO+O_3$ chemiluminescence, a vacuum pump was used to pull the air sample through the reaction chamber at pressure of ca. 10 torr. The reaction chambers are located in a refrigerator and cooled to temperature of 10°C to reduce the dark current of the photomultiplier tubes. These improvements provided a detection limit of NO of 2 ppb with an S/N ratio of 2.

Since the influence of trace impurity NO_x present in diluent gas used for calibration is important in ppb level determination, an elimination technique was examined. This involves the oxidation of NO to NO_2 followed by entrapping the resultant NO_2. O_3 and chromosorb coated with $K_2Cr_2O_7-H_2SO_4$ solution were employed as the oxidizing agent, and silicagel, mixture of sodium carbonate and aluminum hydroxide and active carbon as the entrapping one.

Chemiluminescent reaction

The principal reaction used in the present work is the chemiluminescent reac-

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tion between NO and O_3 ;

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + h\nu$$
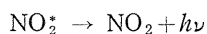
The emission radiated in this reaction is a continuum spectrum extending from 600 nm to 3000 nm. For detection of NO_x ($NO + NO_2$ or the other chemical forms of oxidized nitrogen), a prior conversion of NO_x to NO is required. This is performed through a thermal converter by a catalytic decomposition.

Instrument

The schematic diagram of the NO and NO_x detection system is illustrated in Fig. 1. It is fitted with three inlets, one for the sample gas and the others for
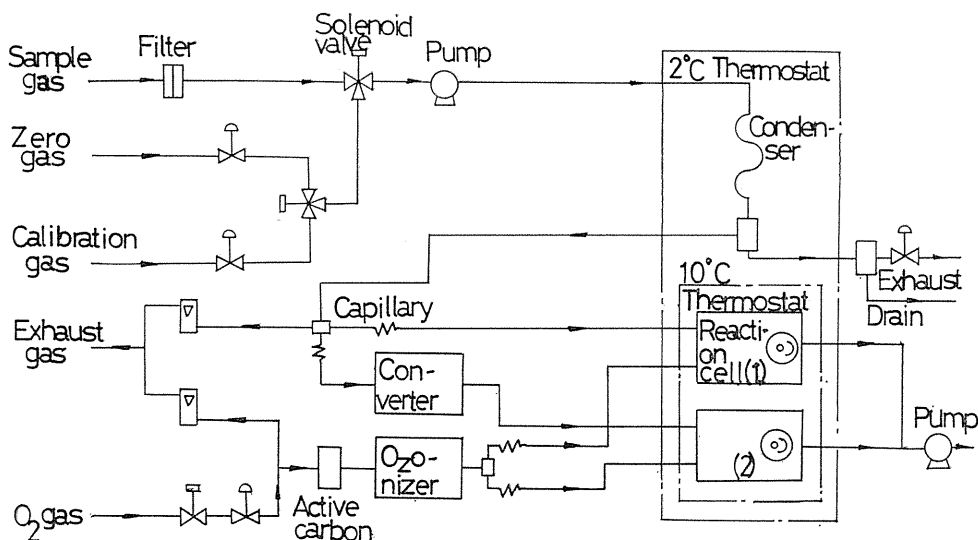

Fig. 1 Schematic diagram of NO-NO_x detection system.

the calibration gas and the zero adjusting gas respectively. The flow path to the reaction cells is chosen by solenoid valves. The sample gas, after filtration of dust and condensation of moisture, is introduced into a reaction cell at a flow rate of 220 ml/min through a capillary tube. Through the capillary tube, another flow is supplied into a NO_x-NO converter in which NO_x is decomposed on a molybdenum catalyst heated at 400℃. The resultant NO is carried into another reaction cell. Both cells are attached with a photomultiplier tube R375 (Hamamatsu TV Co., Ltd.). To avoid the interference by chemiluminescent light below 600 nm radiated by a certain reaction between organic substance and ozone, an optical filter is located between the cell and the photocathode. The photomultiplier tubes are operated at

a low temperature of 10℃ to reduce the thermal noise and the cells at a reduced pressure of 10 torr to eliminate the quenching effect by air.   The other reactant O_3 is prepared through a silent discharge chamber into which O_2 gas is supplied at a flow rate of 35 ml/min, and pulled into the reaction cells.   The signal correponding to NO_2 is put out by subtracting the NO signal from the NO_x one.   Standard gas in different concentration was prepared by a SGGU-72K Diluter (Standard Technology Co., Ltd.).   The diluter comprises of stainless steel capillaries, through which raw NO gas or known diluted gas are diffused into nitrogen gas.   A pure NO gas and a diluted gas of 101 ppm were used to prepare several concentration gas of ppm level and ppb level, respectively.   All pipings were done with teflon tubes of 6 mm o. d..

Experimental

The detection system was calibrated as follows.   Introducing nitrogen gas, the instrumental responce was adjusted to be zero.   Then a standard NO gas of 17 ppm was introduced and it was calibrated to be 17 ppm by fitting the amplifier gain. After this, the responses corresponding to lower concentration were checked.   The result indicated that the response was linear from 20 ppb to 17 ppm and that a detection limit 2 ppb was presented with S/N ratio of 2.

Effect of Trace Impurity NO_x in Diluent Gas

Fig. 2 shows that the measured working curve lies below the expected one at concentration of ppb level.   To confirm this fact, the integrated response for an hour was observed and gave the same result as shown in Fig. 3.   This shows also
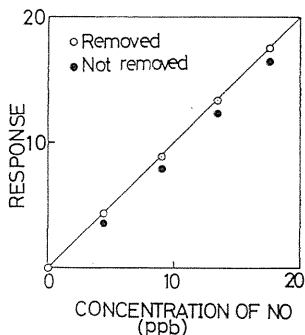

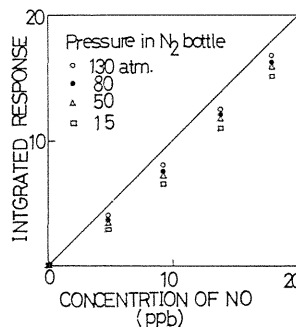Fig. 2 Effect of trace impurity NO_x on response.

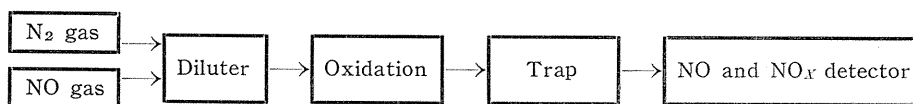Fig. 3 Effect of trace impurity NO_x on integrated response.

the change in the response with the pressure variation in a nitrogen bottle.   From these results, it may be suggested that the trace impurity NO_x present in the nitrogen gas lowers the NO concentration and that the NO_x concentration increases

as the nitrogen gas in the bottle is consumed. The possible cause may be the reaction $NO + NO_2 \rightarrow N_2O_3$ or the quenching effect by NO_2. However, more precise examination is required.

As well as the nitrogen gas, air (mixture of nitrogen and oxygen) was examined as the diluent gas. This is important in a sense that air is the matrix around us. The same linearity as with nitrogen was presented but when it was mixed with the raw NO gas, the rapid oxydation of NO_2 took place.

Elimination of Impurity NO_x

To remove the effect stated above, an elimination procedure[5-7] of trace NO_x in the diluent gas was studied. It involves the oxidation of NO to NO_2 followed by the entrapping the resultant NO_2 according to the following diagram.

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┌──────────┐
│  N₂ gas  │ ──→
└──────────┘      ┌─────────┐   ┌──────────┐   ┌──────┐   ┌──────────────────────┐
                  │ Diluter │→  │ Oxidation │→  │ Trap │→  │ NO and NOₓ detector  │
┌──────────┐      └─────────┘   └──────────┘   └──────┘   └──────────────────────┘
│  NO gas  │ ──→
└──────────┘
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To avoid moisture, gas or solid agents were selected for both the oxidizing and the entrapping reagents.

As the oxidizing agent, O_3 and chromsorb coated with $H_2SO_4 + K_2Cr_2O_7$ were employed. O_2 gas was supplied into an ozonizer incorporating a UV mercury lamp (Toyo Electronic Industrial Co., Ltd.) fitted with reaction chamber of quartz. The yield of O_3 was 0.15 to 0.18 % at oxygen flow rates of 15 to 40 ml/min., which was determined by dissolving the produced gas into a 0.05 N KI solution and titrating the resulting iodine with a N/1000 $Na_2S_2O_3$ solution. The oxidation was performed in a reaction chamber of 500 ml at the room temperature. The excess O_3 was entrapped through a glass tube containing 60 g of solid KI and no O_3 was detcted at the exit portion of the glass tube. Fig. 4 illustrates the result of the oxidation efficiency. NO is converted to NO_2 and not detected if the concentration of O_3 is increased more than twice that of NO. Another oxidizing agent prepared is $H_2SO_4 - K_2Cr_2O_7$. Because of increasing the reaction surface, Chromsorb (20 to 28 mesh) was coated with the oxidizing agent. Dissolve 2.5 g of potassium dichromate into 25 ml of conc. sulfuric acid, mix it with 2.5 g of sieved Chromosorb and heat at 90℃ for half an hour. The titration by a N/10 solution of sodium oxalate gave a $K_2Cr_2O_7$ content of 40%. The substance was packed into a glass tube of 1.2 cm i.d.. From Fig. 5, it is
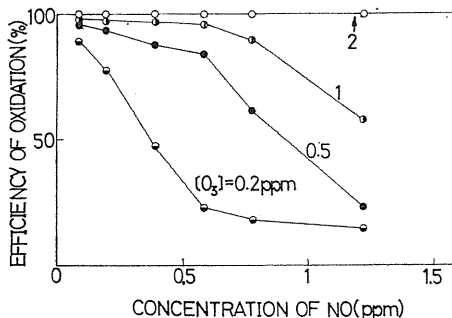

Fig. 4 Oxidation of NO by O_3.

obvious that more than 0. 7 g of the oxidizing converts NO to NO_2 thoroughly.

After oxidation according to the procedures mentioned above, the resultant NO_2 was entrapped by silicagel, sodium carbonate or active carbon.

Silicagel for desiccation was sieved in 6 to 8 mesh and packed into a glass tube of 30 mm i.d.. In Fig. 6, the efficiency of adsorption is shown. For complete
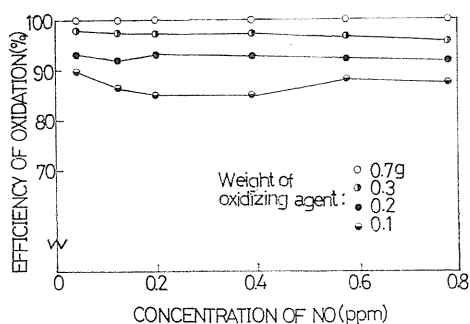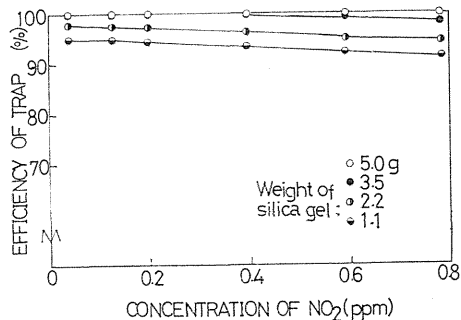

Fig. 5 Oxidation of NO by $K_2Cr_2O_7$-H_2SO_4.

Fig. 6 Adsorption of NO_2 by silica gel.

removal of NO_2 more than 5 g of silicagel was required.

Since NO_2 reacts easily with alkaline reagent, a mixture of sodium carbonate and aluminum hydroxide was studied as the entrapping agent. Dissolve 15 g of sodium carbonate into 1 liter of pure water and introduce carbon dioxide gas into the solution on a water bath at 40℃. Filter the precipitate and dry it at 80℃, followed by shattering, sieving in 20-28 mesh and packing into a glass tube in 30 mm i. d.. It is seen from Fig. 7 that more than 25 g of this agent is necessary to reduce NO_2 of the concentration up to 0. 8 ppm.

Coconutshell charcoal was also inquired as the entrapping agent. After sieving in 20 to 28 mesh, activate at 600℃ under purging with nitroge gas and pack into a glass tube in 30 mm i. d.. As found from the Fig. 8, the efficiency of this adsorbent is higher than those of the substances descrived above.
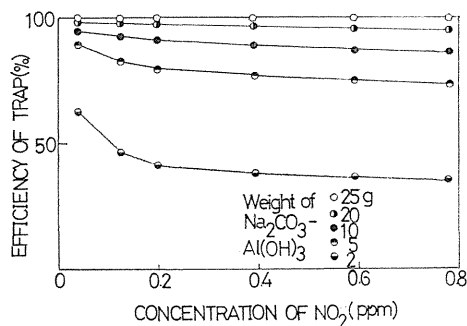

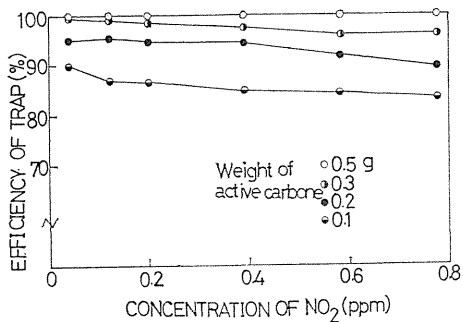Fig. 7 Absorption of NO_2 by
        Na_2CO_3-$Al(OH)_3$.

Fig. 8 Adsorption of NO_2 by active carbon.

Adsorption of NO by Active Carbon

A procedure to eliminate NO without the conversion to NO_2 is also discussed. As is indicated in Fig. 9 which is obtained under the same condition as the elimination of NO_2, NO is adsorbed less than NO_2. However, 11.2 g of active carbon is enough to eliminate most of NO successfully.
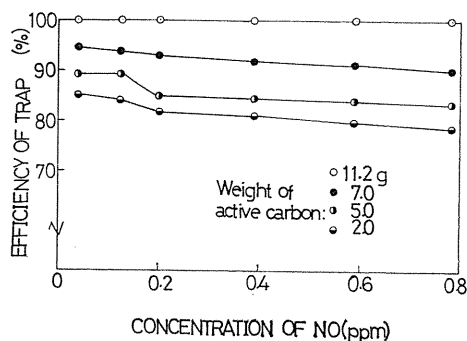

Fig. 9 Adsorption of NO by active carbon.

Effects of Elimination of Trace NO_x in Diluent Gas

To make sure of the effect, the oxidation and entrapping chambers containing 1 g of the solid oxidant and 10 g of silicagel respectively were located between the bottle of nitrogen and the diluter.   The fact that the zero point of NO signal was reduced by 1.5 ppb corresponds to the presence of the trace NO in the diluent gas. Fig. 2 depicts the comparison between the calibration curves before and after the present treantment.   The latter concurs with the theoretical curve, which suggests that the influence of the trace impurities was reduced.

In conclusion, we designed a NO and NO_x detection system for the ambient analysis and obtained a detection limit of 2 ppb.   In determination of low concentrations of ppb level, the effect of the trace impurity NO_x present in the diluent gas used for the calibration of the system was important.   Consequently, some elimination procedure of the impurity was required.   The oxidizing and entrapping technique was examined and found to be suitable for the purpose.

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