A Low-Cost System for Measuring ppb-Level NO₂*

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SUMMARY

A low-cost system to measure low-level nitrogen dioxide (NO₂) in an atmosphere was developed. Its major component included a sensor comprising filter paper treated with 3,3'-dimethylbenzidine (*o*-tolidine), a compound that reacts with NO₂ to generate color proportional to the NO₂ contacted. In addition to the system development, its utility was optimized and the characteristics of the sensor were defined. Originally developed to determine the NO₂ levels during direct-fired tobacco curing, the system may be used to determine the NO₂ levels in other situations. [Beitr. Tabakforsch. Int. 21 (2005) 390–401]

ZUSAMMENFASSUNG

Ein kostengünstiges System zur Messung geringer Mengen von Stickstoffdioxid (NO₂) in der Luft wurde entwickelt. Die Hauptkomponente des Systems bestand aus einem Sensor, der mit 3,3'-Dimethylbenzidin (*o*-Tolidin) behandeltes Filterpapier enthielt. Dies ist eine Verbindung, die mit NO₂ in Abhängigkeit von der aufgetretenen NO₂-Konzentration unter Farbentwicklung reagiert. Zusätzlich zur Systementwicklung wurde die Anwendung optimiert und die Eigenschaften des Sensors wurden beschrieben. Das System wurde entwickelt, um NO₂-Konzentrationen während der Tabaktrocknung unter Direktfeuerung zu bestimmen, es kann jedoch auch zur Bestimmung von NO₂-Konzentrationen in anderen Situationen dienen. [Beitr. Tabakforsch. Int. 21 (2005) 390–401]

RESUME

Un système peu coûteux a été développé pour mesurer les faibles taux de dioxydes de nitrite (NO₂) dans une atmosphère. L'élément principal du système comporte un détecteur équipé de papier filtre traité au 3,3'-diméthylbenzidine

(*o*-tolidine), composé qui réagit avec du NO₂ en générant une coloration en fonction du taux de NO₂ présent. En plus du développement du système, son utilisation a été optimisée et les caractéristiques du détecteur ont été décrites. Ce système a été d'abord conçu pour déterminer les teneurs en NO₂ dans les tabacs séchés au feu, mais ce système peut également être utilisé pour déterminer les taux de NO₂ dans d'autres situations. [Beitr. Tabakforsch. Int. 21 (2005) 390–401]

INTRODUCTION

Several aromatic amines may be used to detect nitrogen dioxide (NO₂) by color reactions. By detecting the color change induced by NO₂ on filter paper impregnated with such a compound, 3,3'-dimethylbenzidine (*o*-tolidine), it was found that NO₂ could be detected. The calibration curve between NO₂ levels and absorbance changes at peak wavelength showed good linear relationships, indicating the possibility of measuring ppb-level NO₂. Finally, a comparison between the method described herein and a reference method indicated that NO₂ at ppb-levels could successfully be measured. In addition, a low-cost opto-electronic system for efficiently measuring ppb-level NO₂ in environmental air or exhaust gases by colorimetry was designed.

DEVELOPMENT OF THE SYSTEM

Nitrogen oxide (NO_x), the term used to describe the sum of nitric oxide (NO), nitrogen dioxide (NO₂) and other oxides of nitrogen, is formed by combustion of fuels and is one of the main components of environmental pollutants involved in acid rain and photochemical smog. Because NO_x significantly impacts human health, much current research is devoted to quantitatively determining the atmospheric NO_x level and reducing it. A prerequisite for NO_x level reduc-

tion is the ability to determine accurately its levels in ambient air, levels which typically are in the low-ppb range. Instruments for NO_x detection have been developed utilizing chemical luminescence (1) and an optical gas sensor (2). Even though these are considered sensitive and accurate, they are too expensive, fragile and complicated to be used as instruments on-site tests. Other devices include badges, tapes, and tubes to capture the NO_x for subsequent colorimetric analysis (3,4). Their disadvantage is that they cannot be utilized to monitor real-time NO_x concentrations in the field. Some convenient, inexpensive personal indicator devices have been developed for detecting NO_x. However, their accuracy and detection are limited (5,6).

When fuel burns at high temperatures, NO_x is formed. Its two major sources are transportation (motor vehicles) and stationary fuel combustion (electric utilities, industrial boilers). The most significant component in NO_x is NO₂. NO₂ is a brownish, highly reactive gas, present in urban atmospheres. It is formed by oxidation of NO in the NO_x emissions. NO₂ is reported to be highly toxic to humans, irritating the lungs, inducing bronchitis and pneumonia, and lowering resistance to respiratory infection. NO₂ is important in both ozone and acid rain generation, both of which are detrimental to terrestrial and aquatic ecosystems. In addition to its reduction, the detection of NO₂ is important. Various instruments for the detection of NO₂ have been developed. They involve chemical luminescence, optical gas sensors, and colorimetric methods (1,2). While these instruments are sensitive and accurate for detecting NO₂, they have disadvantages with regard to cost, convenience and size. Compact and low-cost systems to detect NO₂ have recently been developed. They include an amperometric NO₂ sensor (7), an opto-electronic unit with optical fibers (8), and another type of opto-electronic system with porous glass (9,10). Thus, many studies (1,2,7–10) have been conducted to develop systems for NO₂ detection to ultimately reduce the NO₂ level in environmental air or exhaust gas.

In the study described herein, a low-cost opto-electronic system and method for measuring ppb-level NO₂ with filter paper impregnated with a colorimetric reagent was developed. Colorimetric reagents sensitive to NO₂ include 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (APOX), sulfanilamide (SFA), *N,N*-dimethyl-1-naphthylamine (DMNA), and 3,3'-dimethylbenzidine (*o*-tolidine). It has been reported that *N,N'*-diphenylbenzidine also provides a color reaction with NO₂ (11).

o-Tolidine was selected as the colorimetric reagent in the present study. It was applied to the newly developed device designed to efficiently increase the sensitivity of the color sensor through forced constant-flow and then diffusion of NO₂. It is a simple, low-cost system for *in-situ* colorimetric measurement of ppb-levels NO₂ in environmental air or exhaust gas. The constant forced flow of low levels of NO₂ through the device induces a reaction with the *o*-tolidine deposited on a filter paper substrate. As the gas diffuses through the treated substrate, the reagent color changes in proportion to the NO₂ level. By measurement of the color change with an opto-electronic system, the NO₂ concentration is determined quantitatively.

In the study of this newly developed instrument for NO₂ detection, an attempt was made to optimize some adjust-

able factors affecting the reproducibility and life-time of the chemical sensor, its capacity on upper detection limit, continuous measurement, and the sensitivity of the device, which should be identified prior to application to the field test.

Initially, the instrument was developed to monitor NO_x, particularly its NO₂ content, in indirect-fired tobacco-curing barns. Green tobacco contains little tobacco-specific nitrosamines (TSNAs). Research conducted during 1998 and 1999 showed that NO₂ generated in modern direct-fired curing barns fueled with propane contributes to TSNA formation during flue-curing of tobacco (12,13). TSNAs are classified as potent animal tumorigens even though none has induced respiratory tract tumors when administered via inhalation. To reduce or eliminate TSNA formation in tobacco during flue-curing, substantial reduction of the NO₂ level is considered necessary despite the fact that the mainstream smoke condensates from cigarettes made from flue-cured tobacco with normal and reduced levels of TSNAs show no significant difference in their biological effect (Neutral Red cytotoxicity, Ames test mutagenicity with several *Salmonella typhimurium* strains) (14). Periodic monitoring of NO₂ levels during curing is considered essential in the maintenance of curing equipment. Therefore, it needed to be supported by development of an NO₂ detecting system which offers a low-cost, compact, convenient and accurate method of measurement. Since the system herein described is successful in measuring ppb-level NO_x in tobacco-curing barns, it may be extended to other industrial sites.

Materials and methods

Commercial-grade *o*-tolidine was employed without further purification. Whatman filter paper (No. 4) was used as the sensor base for detecting NO₂. A 5 g/L solution of *o*-tolidine in ethanol was used to impregnate the filter paper by a 5-min immersion in the solution. The *o*-tolidine solution-impregnated filter paper was evaporated to dryness under reduced pressure at room temperature for 1.0 h. Then, the filter paper was stored in desiccators in the dark. Commercial-grade NO_x (National Specialty Gases, Raleigh, NC) was used as the standard (Table 1).

To determine the optimal peak wavelength in the absorption spectrum for the *o*-tolidine-treated filter paper, a Near-Infrared System was used. The experimental tobacco-curing barn where the burner exhaust gas and atmospheric air are introduced and mixed was prepared for comparison of the present method with a reference method. The true NO₂ level of exhaust gas in the experimental tobacco-curing barn was measured by a chemiluminescence analyzer (Model 42, Thermo-Environmental Instruments, Inc.).

Table 1. Standard NO_x used for determining the calibration line

NO _x level, ppm	NO ₂ level, ppm	NO level, ppm	N ₂
4.690	0.230	4.460	Balance
2.738	0.188	2.550	Balance
1.334	1.296	0.038	Balance
1.179	0.117	1.062	Balance
0.854	0.110	0.744	Balance

Figure 1. Schematic diagram of the opto-electronic system for measuring ppb-level NO₂ (A); detailed figure of main body [5] (B): [1] pump; [2] flow-meter; [3] direction of flow of NO₂; [4] box for black; [5] main body; [6] LED; [7] phototransistor; [8] signal flow; [9] signal conditioning circuitry; [10] signal display; [11] lid; [12] metal piece for building up the top of the main body, and providing a seat of the lid; [13] opening for the sensor holder; [14] sensor holder; [15] hole for the diffusion of nitrogen dioxide gas; [16] O-ring; [17] place for screw; [18] box for the flow of nitrogen dioxide gas, and equipped by opto-electronic system; [19] place for LED; [20] place for phototransistor; [21] binder for fixing the sensor holder; [22] guide; [23] hole for the flow of NO₂.

Opto-electronic system for measuring ppb-level NO₂

The newly designed system, diagramed in Figures 1A and 1B, comprised three parts: 1) a sampling part for introducing NO₂ into the main body [5], 2) a sensor holder for the color reaction, and 3) an opto-electronic detector to measure the color change on the sensor.

To increase the instrument sensitivity to NO₂, the sample gas is forced through the main body of the device by a small pump. As a result, the diffusivity of NO₂ gas through the opening [15] of the sensor holder can be increased. The detailed components of this part consist of a pump [1], flow-meter [2], main body [5], tubes, and side-holes of the main body [23]. The pump is set downstream from the main body to pull the NO₂ through the main body to prevent contamination by the pump. The gas flow direction is shown by symbol [3], Figure 1A. Because the flow-rate during sampling affects the intensity of the sensor color change, the flow-meter for constant flow of sample gas must be set prior to the pump. Also, the pattern of gas flow inside the main body affects sensitivity, so enough space for the flow of sample gas between the sensor holder [14] and cylinder bars with small hole for fixing LED [6] or phototransistor [7] is necessary. It is important that openings such as [13], [19] and [20] in the main body be completely protected from air leaks. Because the pump draws the NO₂ for sampling into the main body, an air leak causes the contamination of sample gas by environmental air outside the room for test. Therefore, the top of the main body is built up by another piece of metal [12] to originally remove air leaks problem from the instrument. It is tightly fixed on the top with a gasket for sealing by screws. The lid [11] of the main body is specially designed for sealing the overlapping structure with a metal piece [12], and screwed tight during test. The small holes for fixing LED and phototransistor in cylinder bars must also be sealed.

Next, the sensor holder [14] in this instrument is designed to support the sensor, promote the color reaction on the sensor by the NO₂ diffusion through both side holes, and provide a pathway for light emitted from the LED for the detection of color change. Also, the size of this holder is necessary for convenience when installing the sensor and placing the holder in the box [18] through its opening [13]. The O-ring [16] between both sides of the holder is compressed by screws [17] so that the color reaction on the sensor is caused by no other NO₂ flow except the perpendicular diffusion-flow through holes [15] of both sides of the holder. The binder [21] is used for fixing the sensor holder [14] inside the box [18], and the guide [22] is used to align the centerlines between sensor holder holes [15] and box holes [19, 20].

Finally, the color change caused by the NO₂-sensor reaction is quantified by the opto-electronic detector with its LED [6] and phototransistor [7]. Monochromatic light at wavelength 470 nm and fixed intensity is generated by LED, penetrates through the treated paper, and is finally detected by the phototransistor. This signal [8] is amplified and conditioned by signal conditioning circuitry [9] before being displayed on the LCD [10]. Fundamental to the development of this device was the determination of the optimum wavelength of light from the LED that would provide the greatest sensitivity to the color change. During development of the device, experiments were conducted to determine the optimum wavelength. For example, with *o*-tolidine as the reagent, Figure 2 shows that light with wavelength of about 430 nm is most sensitive to the color change. Furthermore, the device must be shielded from external light to eliminate extraneous noise to the opto-electronic system. The duplicate box [4] outside the main body [5] is used to prevent penetration of external light.

Figure 2. Visible-light absorption spectra of three kinds of filter paper

Figure 3. Calibration line for determining NO₂ level in the sampling gas with the opto-electronic system protocol

Results and discussion

To utilize the system, the calibration line of NO₂ was determined. A single sheet of *o*-toluidine-treated filter paper was exposed for 10 min to several different concentrations of NO₂, flow-rate 1000 cc/min. The absorbance change of monochromatic light (defined as the difference between the absorbance of unexposed treated filter paper and that of the NO₂-exposed treated filter paper) was then calculated by measurement of the intensity of the light traversing the sensor. From this, a corresponding calibration curve (Figure 3) was obtained. This curve shows that the absorbance change is linearly proportional to the NO₂ level.

$$y = 0.0751x + 0.0122 \text{ with } R^2 = 0.9876$$

where y = absorbance change of the sensor, x = NO₂ level. Not only can the calibration line define the concentration of NO₂ in the sample but also the real-time monitoring of the ppb-level NO₂ in the field can be accomplished.

An experimental burner-equipped tobacco-curing barn was employed to compare results from the currently described system with those from the chemiluminescence analyzer. The sample gases were introduced continuously into the instrument for 10 min at a flow-rate of 1000 cc/min. To cool the sample gases from the experimental barn, the simple cooler was set prior to the instrument. Even though an attempt was made to fix the NO₂ level of sample gases from the chemiluminescence analyzer at a single value for 10 min, it was difficult to do so. Thus, because there were some fluctuations of the values measured by the chemiluminescence analyzer (Figure 4), the average NO₂ concentration for 10 min was employed in the comparison. After comparing those values, Figure 5 showed that some

Figure 4. Temporal changes of NO₂ levels of the sampling gas from the experimental barn, measured with the chemiluminescence analyzer

Figure 5. Comparison between NO₂ levels (<2.5 ppm) measured by the instrument described herein and the chemiluminescence analyzer reference method

differences occur between the methods, especially at an NO₂ level greater than 1.5 ppm. It is considered that those results are produced by the following two factors: 1) An NO₂ level higher than 1.5 ppm is beyond the range of the calibration line. 2) Because the colorimetric reagent, *o*-toluidine, on the filter paper should be entirely consumed within 10 min by NO₂ at a level greater than 1.5 ppm, there is no further color reaction on the sensor to cause the underestimate. Even though standard NO_x with an NO₂ level higher than 1.5 ppm was not directly employed to determine the reason, temporal reduction on the slope of absorbance changes continuously measured on the single filter paper impregnated with 5 g/L of *o*-toluidine in ethanol (Figure 6) indirectly showed the reason. Therefore, it is necessary to prepare sensors with higher concentrations of *o*-toluidine to measure NO₂ levels above 1.5 ppm. Figure 7, except for two data points with NO₂ levels greater than 1.5 ppm, showed better agreement between them. Thus, it indicated that NO₂ at ppb-level was successfully measured by the method and device described herein.

Conclusions

By detecting color change induced by NO₂ on filter paper impregnated with the colorimetric reagent *o*-toluidine, it was found that NO₂ could successfully be detected. The

Figure 6. Temporal changes of absorbance continuously measured on a single filter paper impregnated with *o*-tolidine-ethanol solution (5 g/L) by the instrument described herein into which 1.296 ppm NO₂ flowed at 1000 cc/min

Figure 7. Comparison between NO₂ levels (<1.5 ppm) measured by the instrument described herein and the chemiluminescence analyzer reference method

calibration line between NO₂ levels and absorbance changes at peak wavelength showed good linear relationships which indicate the possibility of measuring ppb-level NO₂. Also, it was found that after comparison between NO₂ concentrations inside the experimental tobacco-curing barn measured by the method described herein and by the chemiluminescence analyzer, NO₂ at a ppb-level was successfully measured. Thus, in this study, a low-cost opto-electronic system for efficiently measuring ppb-level NO₂ in environmental air or exhaust gases by colorimetry was developed.

OPTIMIZATION OF THE SYSTEM

As described above, a low-cost opto-electronic system for efficiently measuring ppb-level NO₂ in environmental air or exhaust gas by colorimetry was developed. Prior to application to the field test, the next step was to identify those adjustable factors affecting the reproducibility and life-time of the sensor (the *o*-tolidine-treated filter paper), the measuring capacity, the continuous measurement, and the sensitivity of the sensor. To increase those capacities of the device, the identified factors must be simultaneously optimized. From them, several adjustable factors such as

Figure 8. Opto-electronic system for determining NO₂ level

deviation among the sensors produced by the same method, lifetime of the sensor, concentration of colorimetric reagent in the solution, dipping time of filter paper in the solution, sampling time, and sampling flow-rate were ascertained. Additionally, the effect on sensitivity of the NO level in the sample gas needed to be determined.

Materials and methods

Sensors were prepared with Whatman filter paper and *o*-tolidine concentrations of 3 g/L, 5 g/L, 10 g/L, and 20 g/L as described above. As before, the *o*-tolidine-treated filter paper was dried under reduced pressure at room temperature but various drying periods were used. Each sensor was then stored in the dark. The standard NO_x was that described in Table 1.

In this phase of the study, the effect of a voltage adjuster of power to the LED with an upper 12-V limit to emit the light with a wavelength of 470 nm attached to the opto-electronic system (Figure 8) for NO₂ detection was tested as was the volumetric flow controller of NO_x from the cylinder.

Results and discussion

Reproducibility and life-time of the chemical sensor: To determine the reproducibility of the sensors, they were impregnated with a 20 g/L ethanol solution of *o*-tolidine for 10 min, and then their initial light intensities were measured by the LED (input power, 10 V) and phototransistor. After 10-min exposure to 0.230 ppm NO₂ at a flow-rate of 1000 cc/min, the sensitivity of the sensors was measured in the system. Figure 9 depicts the results obtained with 10 similarly prepared sensors. The relative standard deviation of response ($n = 10$) as an index of reproducibility was 6.8% for the initial light intensity, 10.3% for the sensor sensitivity. The initial light intensity of the sensor is related to the amount and uniformity of the impregnated colorimetric reagent in the sensor, and so its higher reproducibility is very important to finally raise the reproducibility of the sensitivity.

Several tests on the change in reproducibility of the sensitivity of the sensor with time were conducted to determine its life-time. Similarly prepared sensors were stored in a vinyl bag in the dark under other room conditions. Their sensitivities were measured day by day at two levels of

Figure 9. Distribution of the initial light intensities of 10 similarly prepared chemical sensors and their sensitivities when exposed to 0.230 ppm NO₂, flow rate 1000 cc/min

Figure 10. Temporal changes of the sensitivities of stored chemical sensors

NO₂, 0.110 ppm and 1.296 ppm. The results (Figure 10) show that the sensitivities of sensors stored in a vinyl bag were unstable, especially those at 0.110 ppm NO₂. They became quite unstable in one day. It was considered that the long-term exposure of sensors to NO₂ (8–30 ppb) included in the vinyl bag or the NO₂ that penetrated the bag film from environmental air lowered their sensitivities at particularly low NO₂ concentrations. Therefore, a machine and film for vacuum packaging were employed to protect the sensors from exposure to environmental NO₂ during long-term storage. This resulted in sensitivity stability for about 9 days after *o*-tolidine treatment. Even though the sensitivity of the sensor exposed to 1.296 ppm NO₂ was maintained well after 9 days, that at 0.110 ppm NO₂ disappeared (Figure 10). Also, the variance of sensitivities at lower NO₂ concentrations was much greater than that at higher NO₂ concentrations for the same period.

Capacity on upper detection limit, continuous measurement and sensitivity of the sensor: In this phase of the study, an attempt was made to increase not only the sensitivity of the sensor but also its capacity for upper detection limit and continuous measurement. In fact, because the two are not proportional, they should be optimized for practical purposes. To increase the sensor capacity for upper detection limit and continuous measurement, the *o*-tolidine level in the sensor should be raised by increasing the *o*-tolidine solution concentration and dipping time of the sensor into the solution or by decreasing the time interval of ethanol removal from the sensors and the sample gas flow-rate.

Figure 11. Temporal changes of absorbance changes of sensors treated with two concentrations (3 g/L, 20 g/L) of *o*-tolidine solution for 10 min, dried for 40 min, then exposed to (A) 0.110 ppm NO₂, flow-rate 1000 cc/min; (B) 1.296 ppm NO₂, flow-rate 1000 cc/min; (C) treated with *o*-tolidine solution (20 g/L) for 5 min, dried for 40 min, then exposed to 0.110 ppm and 1.296 ppm NO₂, flow-rate 1000 cc/min; (D) treated with *o*-tolidine solution (20 g/L) for 10 min, dried for 20 min, then exposed to 0.110 ppm and 1.296 ppm NO₂, flow-rate 1000 cc/min

1) As seen in Figures 11A and 11B, sensors treated with the higher concentration *o*-tolidine solution (20 g/L) showed higher sensitivity. Obviously, sensors treated with the higher concentration solution of *o*-tolidine have more *o*-tolidine to react with NO₂. Thus, the higher sensitivity sensor provides the equipment with a more stable sensitivity for detecting higher levels of NO₂. It was deduced that the capacity of the sensor for upper detection limit and continuous measurement is dependent on the *o*-tolidine concentration in the solution.

Figure 12. Absorbance changes of sensors treated with *o*-tolidine solution (20 g/L) for 10 min, dried for 40 min, then exposed for 10 min to 0.110 ppm and 1.296 ppm NO₂ at various flow-rates

Figure 13. Relationship between power voltage to LED and initial light intensity of the sensor

2) The dipping time of the sensor in the solution during its preparation little affected the capacity of the sensor on upper detection limit and continuous measurement (compare Figures 11A, 11B, and 11C). It is assumed that the sensor could be saturated by the solution within 5 min. If the NO₂ level is measured once, not continuously by our meter, Figures 11B and 11C indicate that the optimum sampling time for each test is 10 min within which time the temporal changes maintain linearity even at a flow of 1.296 ppm NO₂. 3) The time interval of ethanol evaporation from the sensors under reduced pressure was quite important to measure NO₂ level continuously. In Figure 11D, both temporal changes at 20-min drying time showed much better linearity than those in Figures 11B and 11C at 40-min drying time. The calculated absorbance changes per unit NO₂ concentration and unit time at 0.110 ppm and 1.296 ppm NO₂ were 0.00882 and 0.00802 (abs/ppm/min), respectively, and the two values were quite close. This indicates that the NO₂ level can be continuously measured by the coefficients for at least 30 min.

4) Figure 12 showed that the increase of flow-rate of NO₂ raised the level of sensitivity of sensors as expected. However, because this increase consumes much of the sensor *o*-tolidine, the lower flow-rate of sample NO₂ is considered to be better for increasing the sensor capacity on upper detection limit and continuous measurement. It was reported that the diffusion resistance of NO₂ through the gas film could be neglected for a gas flow-rate greater than 300 cc/min (7). However, because the NO₂ flow in the experimental prototype was unstable at a flow-rate below 1000 cc/min, the optimum flow-rate for the current device was considered to be 1000 cc/min.

Figure 14. Absorbance changes of sensors treated with (A) various *o*-tolidine solutions (3 g/L, 5 g/L, 10 g/L, 20 g/L) for 10 min; (B) *o*-tolidine solution (20 g/L) for various dipping times, dried for 40 min, then exposed for 10 min to 0.110 ppm and 1.296 ppm NO₂, flow-rate of 1000 cc/min

Figure 15. Effects of NO on instrument sensitivity

In fact, the sensitivity of the instrument described herein is affected mainly by two factors, the opto-electronic part and the sensor. First, the opto-electronic part including the LED and phototransistor strongly affected the instrument sensitivity. In Figure 13, the initial light intensity of the sensor related to the sensitivity was increased proportionally with power voltage to the LED. Otherwise, the concentration of *o*-tolidine in the solution and dipping time of the sensor in the solution also affected the sensitivity of the developed instrument (see Figures 14A and 14B). From them it can be seen that the optimum solution concentration of *o*-tolidine was about 10 g/L, the optimum dipping time about 10 min.

NO effect on the sensitivity: To determine the effect of NO on the sensitivity, tests were carried out with standard NO_x (Table 1). The result (Figure 15) indicated that the other three points with over 1.0 ppm NO were shifted from the line connecting both end-points with relatively less NO.

Figure 16. System for measuring effects of temperature and RH on the sensitivity of chemical sensors in the artificial environment

The magnitude of variation between them was proportional to the NO in each standard. This indicates that the instrument sensitivity was only slightly affected by NO. However, because the NO_x (which included about 1.0 ppm NO) showed a sensitivity change of less than 0.005, it was concluded that NO has little effect on the results obtained with the instrument described herein when it is used to monitor low-level NO_x.

Conclusions

This phase of the study involved the determination of the adjustable factors that affect the reproducibility and life-time of the sensor (the *o*-toluidine-treated filter paper), the measuring capacity, the continuous measurement, and the sensor sensitivity. Also, the identified factors were simultaneously optimized to increase those capacities of the device. The relative standard deviation of response ($n = 10$) as an index of reproducibility was 6.8% for the initial light intensity and 10.3% for the sensor sensitivity. About the life-time of the sensor packed by the vacuum machine, the sensor sensitivity at 1.296 ppm NO₂ was maintained well after 9 days, but that at 0.110 ppm NO₂ disappeared. Also, the variance of sensitivities under lower concentration of NO₂ was much greater than that under higher concentration of NO₂ over the same period.

It was found that the sensor capacity for upper detection limit and continuous measurement is dependent on the *o*-toluidine solution concentration. However, the time of dipping the sensor into the solution little affected the sensor capacity for upper detection limit and continuous measurement. The optimum sampling time for each test is 10 min during which the temporal changes maintain linearity even at a flow of 1.296 ppm NO₂. Also, the time interval of ethanol removal from the sensors under reduced pressure was quite important to the continuous measurement of NO₂ level. The increase of sampling flow-rate of NO₂ raised the level of sensitivity of sensors as expected.

With regard to the sensitivity of the instrument, the optimum concentration of *o*-toluidine in the solution was about 10 g/L,

the optimum dipping time was about 10 min. Additionally, the level of NO included in the sampling gas affected its sensitivity only slightly with noise less than 0.005.

CHARACTERISTICS OF THE CHEMICAL SENSOR FOR MEASURING ppb-NO₂ BY COLORIMETRY

In this phase of the study, the characteristics of the sensors used in the opto-electronic system described in the sections above were determined. Tests on the life-time of the sensor preserved in a vacuum package indicated its optimum life-time was about 9 days. In addition, the relative standard deviation of absorbance changes of the sensors at lower NO₂ concentration was greater than that at higher NO₂ concentration during storage, because the sensors could be continuously contaminated by ambient NO₂. After the vacuum package of sensors was opened for field tests, the sensitivities of the sensors subsequently stored in a vinyl bag were well maintained for at least 6 h. The effects of temperature and relative humidity (RH) on the sensitivity of the sensor were found to be negative. To apply the instrument described herein to the tobacco-curing process, the optimized coefficient of the calibration line for it was determined. Comparison of NO₂ levels between a reference method and the method described herein indicated good agreement. Also, even though temperature and RH in each phase of the tobacco-curing process varied widely, those phases had a similar coefficient on their calibration lines.

Materials and methods

The sensor (filter paper, *o*-toluidine solution, 20 g/L) was prepared as described above. It was packed by a vacuum machine, then stored in the dark. Commercial-grade NO_x (National Specialty Gases, Raleigh, NC) was used as the standard (Table 1). To determine the effects of temperature and RH on the sensitivity of the sensor, the system in Figure 16 was developed to measure the effects in the artificial environment. The environment in the experimental chamber

Figure 17. Temporal changes of the sensitivities of stored chemical sensors

Figure 18. Temporal changes during storage of the initial light intensities of similarly prepared chemical sensors

was controlled during introduction of the exhaust gas from the burner by means of a temperature and RH controller. Here, propane was the burner fuel. The NO_2 level in the chamber was adjusted by a flow controller attached to the fuel cylinder and an air blower below the burner. The NO_2 level in the chamber was monitored with a chemiluminescence analyzer (Model 42, Thermo-Environmental Instruments, Inc.) as a reference method to the instrument described herein. Temperature and RH were recorded. However, the average NO_2 level measured by the chemiluminescence analyzer was applied for its comparison to our instrument, because those data from inside the chamber actually fluctuated.

Results and discussion

Life-time of the chemical sensor: Similarly prepared sensors were stored in darkness under room conditions and two storage conditions: in a vinyl bag with and without vacuum. Their sensitivities were measured daily with the newly developed instrument described herein at two NO_2 levels (0.110 ppm and 1.296 ppm), flow-rate 1000 cc/min, 10-min exposure. Because of their continuous exposure to environmental NO_2 (8 to 30 ppb), the sensitivities of sensors stored in the vinyl bag without vacuum rapidly disappeared in a day in the experiments with 0.110 ppm NO_2 . However, the sensitivities of sensors stored in vacuum lasted at least 9 days for 0.110 ppm NO_2 . Useable sensitivities lasted about a month at 1.296 ppm NO_2 (Figure 17).

Figure 19. Distribution of initial light intensities of similarly prepared chemical sensors and their sensitivities when exposed to 0.110 ppm NO_2 (A) and 1.296 ppm NO_2 (B)

Calculation of the relative standard deviation of absorbance change as an index of reproducibility (Figure 17) gave a value ($n = 5$) for 0.110 ppm NO_2 of 32.4% and a value ($n = 9$) for 1.296 ppm NO_2 of 18.0%. The sensors showed higher instability over time for detecting lower NO_2 concentration because of their long-term exposure to environmental NO_2 . Also, arithmetically the deviation for lower NO_2 concentration should be more sensitive, assuming the same measuring error. Of the values noted above, the relative standard deviation for 0.110 ppm NO_2 excluded the initial and final data because of their wide deviation from the average. Therefore, to maintain satisfactory sensitivity of sensors under low NO_2 concentration, it is recommended that only those sensors stored between 1 and 9 days be used. Figure 18 showed that the initial light intensity of sensors prior to NO_2 treatment continuously decreased with time during storage. This phenomenon is probably caused by long-term exposure to environmental NO_2 .

For comparison, each initial relative standard deviation of absorbance change at 0.110 ppm and 1.296 ppm NO_2 was determined. The value ($n = 8$) at 0.110 ppm NO_2 was 18.3% (Figure 19A); the value ($n = 8$) at 1.296 ppm NO_2 was 10.1% (Figure 19B). These two relative standard deviations were much lower than values in Figure 17. This indicates that the reproducibility of the sensors was strongly affected by the duration of their storage, especially for detection of lower NO_2 concentrations. The linearity between absorbance change of the sensors and time was unstable during their storage, indicating that continuous measurement would be unstable as well. When the absorbance change of the sensors stored in vacuum for 2 days was measured continuously every 5 min for 30 min under

Figure 20. Temporal changes of absorbance change of chemical sensors stored for 2 days, then exposed to 0.110 ppm NO₂

Figure 21. Temporal changes of the sensitivities of chemical sensors stored in a vinyl bag

the flow of 0.110 ppm NO₂, a bend between 0 and 10 min on the sensitivity was observed (Figure 20). This was considered another obstacle to overcome for continuous measurement.

In fact, it is difficult to preserve the sensors in a vacuum package again once the package has been opened for a field test. Therefore, knowledge was required on how long the sensors in the ordinary vinyl bag maintain their sensitivities. It was determined that they were well-maintained for at least 6 h (Figure 21).

Effects of temperature and relative humidity on the sensitivity of the sensor: Comparison of the data in Figures 22A and 22B indicated that the coefficient of regression equation in Figure 22B was larger than that in Figure 22A. This showed that temperature negatively affected the sensitivity of the sensors under the same RH. Also, the coefficient of regression equation for Figure 22B data was larger than that for Figure 22C data. Thus, RH negatively affected the sensitivity of the sensors at the same temperature. That coefficient of Figure 22D data was even larger than the others, because it was determined with standard NO₂ levels at lower temperature (room temperature) and no moisture.

Application to the tobacco curing process: The instrument described above was originally developed to determine the NO₂ level inside tobacco-curing barns. The tobacco-curing schedule (Figure 23) typically has three phases: yellowing, leaf drying, and stem drying (15). There is considerable difference in temperature and RH among these tobacco-

Figure 22. Absorbance change of chemical sensor vs. NO₂ level in the chamber at (A) 68 °C and 20%; (B) 49 °C and 20% RH; (C) 49 °C and 60% RH; (D) standard NO₂ levels

Figure 23. A typical tobacco curing schedule

Figure 24. Absorbance changes of sensors measured in the experimental chamber at various temperatures and RHs (A) without a cooler; (B) with a cooler

curing phases. However, as described above, temperature and RH both negatively affected the sensitivity of the sensors. Also, the yellowing phase involves low temperature and high RH, whereas the two drying phases involve higher temperature and lower RH. Thus, it was assumed that each phase of the tobacco-curing process has a similar coefficient in the calibration line. In fact, Figure 24A showed satisfactory linearity among the three phases by obtaining a single calibration line including temperature (35–68 °C) and RH range (20–80%) with regard to them. To decrease the temperature and RH of sample gas, a cooler consisting of a

Figure 25. Comparison between NO₂ levels measured without a cooler by the reference method and by the instrument described herein

flask and ice was employed for tests. As expected, the coefficient of the calibration line in Figure 24B was slightly greater than the result without the cooler, but the stability of this method was not better. That was because condensed water in the flask and the temperature lowered by ice melting during long-term experiments caused some errors in the measurement. Figure 25 showed good agreement through comparison of NO₂ levels between the reference method and our developed instrument without a cooler.

Conclusions

We have already developed the low-cost opto-electronic system to efficiently measure ppb-level NO₂ in environmental air or exhaust gas by colorimetry. Because that color change is formed by reaction between NO₂ and a colorimetric reagent (*o*-tolidine) on filter paper as a sensor, it is very important to know those various characteristics.

First, the optimum lifetime of the sensors preserved in a vacuum package was found to be about 9 days, during which their sensitivities at even low NO₂ concentration were well-maintained. In addition, the relative standard deviation of absorbance changes of the sensors at the lower concentration of NO₂ was larger than that of the higher one during storage, because the sensors could be continuously contaminated by ambient NO₂. After unpacking the vacuum package of the sensors for field tests, the sensitivities of sensors stored in a vinyl bag again were well maintained for least 6 h.

It was found that temperature and RH had negative effects on sensor sensitivity. To apply the instrument described herein to the tobacco-curing process, the optimized coefficient of the calibration line for it was determined. Comparison of NO₂ levels determined by a reference method and the method described herein indicated good agreement. Also, even though temperature and RH in each phase of the tobacco-curing process varied widely, the phases had a similar coefficient on their calibration lines.

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