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Development of highly sensitive nitrogen dioxide monitoring device and its application to wide-area ubiquitous network

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ABSTRACT

We have developed an NO_2 sensing device with high time resolution for application to a wide-area ubiquitous network. The NO_2 sensing device employs the colorimetric reaction between NO_2 and diazo-coupling reagents. We estimated the formation and decomposition rate of the azo dye in the sensor elements and found that no decomposition occurred and that the formation rate was fast enough for us to measure NO_2 concentration at 10 min intervals with a detection limit of 12 ppb. We have constructed sensing terminal units containing the NO_2 sensing device, a GPS device, a compass, a switch, LEDs and a wireless terminal unit for a wide-area ubiquitous network. We successfully monitored the outdoor NO_2 level at 10 min intervals using the developed terminal units mounted on a bicycle in certain areas of several cities. We also designed and implemented an application where bicycles collect geo-tagged air quality samples and post them on a map that other cyclists can use to determine their route.

1. Introduction

Nitrogen dioxide (NO_2) is a major air pollutant that is subject to environmental regulation in many countries. In the outdoor environment, NO_2 is mainly emitted from vehicles and factories [1,2]. Its distribution is very localized, and high NO_2 concentrations are detected at the roadsides [3–11]. Although the association between NO_2 and asthma is not clear [12,13], NO_2 clearly has an adverse effect on human lungs [14–21], and the US EPA strengthened the national ambient air quality standard in relation to NO_2 (1 h standard at a level of 100 ppb) [22]. Although there are some air quality forecasts provided by governments [23,24], these forecasts mainly deal with ground level ozone and particulate matter. There are several forecasts for NO_2. However, because the grid scale used in the simulation is large, for example 1–10 km, the forecast concentration is one value per grid [25], and localized NO_2 concentrations cannot yet be forecast.

Recently, the number of people commuting by bicycle has increased, reflecting the fact that people are becoming more concerned about fitness and ecology. For people who commute by bicycles, information about localized air pollutants would be very useful if they wish to select the route with the lowest air pollutant concentrations, and it would help them to avoid the health damage that can be caused by breathing such pollutants. There have been a few reports concerning networks for sensing air pollutants [26–28], however NO_2 monitoring is difficult because of the lack of a small sensitive monitoring device. If we are to realize NO_2 monitoring for bicycle commuters, we need a highly sensitive NO_2 monitoring device (sensitive in urban atmospheres (from few ppb to 100 ppb)) with a high time resolution. There have been many reports dealing with small NO_2 sensing systems, such as an optical fiber transducer based on calixarenes [29], a copper phthalocyanine micro system [30], metal complex ($Cr(bipy)O_2Cl_2$) thin film [31], an N-1 naphthylethylenediamine dihydrochloride sensor [32], a Cr doped TiO_2 gas sensor [33], a porous glass gas sensor [34], an SnO_2 gas sensor [35], azobenzene thin film [36] and passive samplers [37,38]. However, some have insufficient sensitivity for monitoring urban atmospheres, and some have a response time of some that is insufficient for monitoring the changes in the roadside NO_2 concentration over time. In 1998, we developed an NO_2 sensor [39] for monitoring at a fixed point every hour, because environmental NO_2 monitoring using a small sensing device was needed to evaluate roadside NO_2 concentrations. Now wide area ubiquitous network technology has been developed, and we conceived an application where many bicycles collect geo-tagged air quality samples and post them on a map that other cyclists can use to determine their route. Then in this work we estimated the detection limit and time resolution of our NO_2 sensor and developed a small NO_2 monitoring device for application to a mobile sensing network. We then constructed sensing terminal unit containing the NO_2 sensor, a GPS device, a

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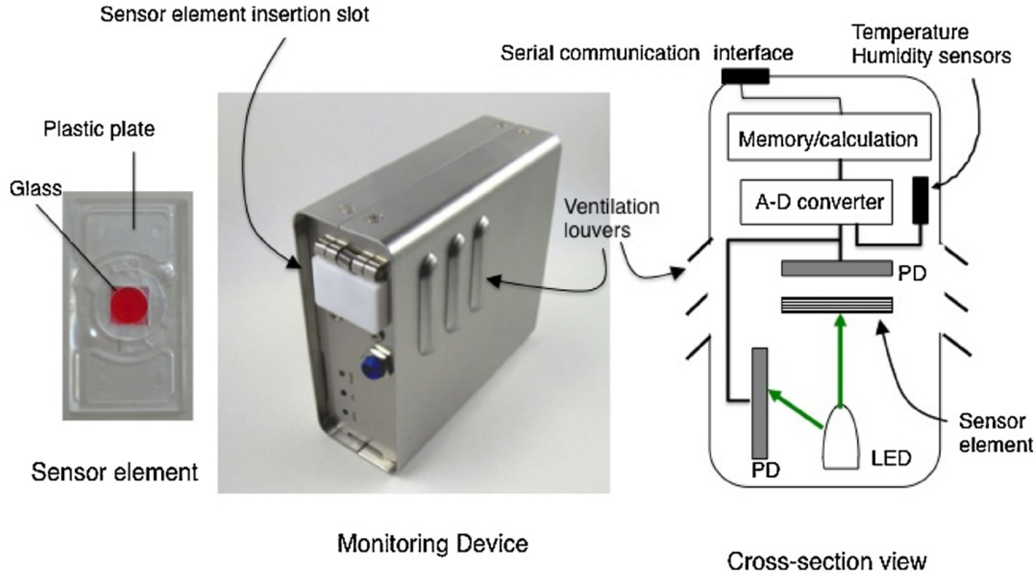

Fig. 1. Photographs of sensor element, monitoring device and cross-section of monitoring device.

compass, a switch, LEDs and a wireless terminal unit for a wide area ubiquitous network and mounted the terminal unit on bicycles to allow us to perform a demonstration experiment in certain areas of Katsushika, Tokyo, Japan.

2. Experimental

2.1. Sensor element preparation and sensor response estimation

The sensor elements were prepared using a previously described method [39]. The reaction between NO_2 and diazo coupling reagents was used to detect NO_2. As a substrate we used a 1 mm thick porous glass sheet with an average pore diameter of 4 nm (AGGK-PG4-S; Gikenkagaku Co. Ltd., Japan). An azo compound with an absorption peak at 525 nm formed as a product of the reaction between the diazo coupling reagents impregnated in the porous glass and the NO_2 in the atmosphere.

To estimate the reaction rate between the diazo coupling reagents impregnated in the porous glass and the NO_2 in the atmosphere, the sensor elements were first exposed to artificial air containing NO_2 at 800 ppb with 50% humidity for 3 min, and then placed in a spectrometer's sample room filled with artificial air without NO_2 and with 50% humidity, and the absorbance change of the sensor element at 525 nm was measured every 30 s. We measured the transmission and absorbance spectra of the samples using a Hitachi U-4100 spectrometer.

2.2. Device

We developed the portable NO_2 sensing device shown in Fig. 1 for a mobile sensing network. Each side of the device was equipped with a pair of louvers to allow air ventilation and to prevent outside light from entering the device. We used an LED (NSPG500DS: NICHIA Co., Japan) emitting at 525 nm as a light source. We used two photodiodes (S1226-44BK: Hamamatsu Photonics K.K., Japan) to detect light intensity; one for the light that passed through the sensor element and the other for the light that did not pass through the sensor element as a reference. This allowed us to measure the absorbance with high accuracy, because the light intensity of an LED usually depends on temperature. Humidity and temperature sensors (SHT75: Sensirion Inc., Japan) were also installed in the device to monitor the NO_2 concentration, temperature and humidity simultaneously. The outputs of the PDs were converted from analog to digital through an A–D converter (ADS8325IBDGK: Bure-Brown Co., US) and the NO_2 concentration was calculated using the digital signals. It was very compact at 100 mm × 100 mm × 40 mm (D × H × W). The power source was a dry-cell battery.

2.3. Gas exposure and measurements

To estimate the detection limit, we pumped outside air into a chamber containing a fan to agitate the air. The chamber was set in an experimental room. The developed device was installed in the center of the chamber and measured the hourly NO_2 concentration in this air. The NO_2 concentration in the chamber was simultaneously analyzed by a Japan Thermo-Electron (JTE) analyzer model 42C. Next we examined the correlation between average NO_2 concentration over 10 min measured with our developed device and with the commercial analyzer in an actual outdoor environment. The outline of the experiment is shown in Fig. 2. We pumped outside air into a chamber connected to the JTE analyzer. On the other hand, we placed our developed device in a protective housing with windows on both sides, and the housing was mounted horizontally on utility poles at a height of 2.25 m above the ground. We measured the correlation between the average NO_2 concentration over 10 min indicated by our device and by the JTE analyzer.

2.4. Environment monitoring terminal unit

We developed an environmental monitoring terminal unit containing the NO_2 sensing device, a switch, a compass (RDCM-802, GEOSENSORY, Australia), a GPS device (GT-720F, CanMore Electronics Co. Ltd., Taiwan), and a wireless gateway based on Mote (MX2110J, Crossbow Japan Ltd., Japan) as shown in Fig. 3. Each part of the terminal unit could connect through an IEEE802.15.4 2.4 GHz wireless network, therefore the layout of the parts was flexible. The terminal unit was designed to be mounted on a bicycle. The compass and the GPS device were used to obtain the direction in which the person was riding the bicycle, and the position of the bicycle. The switch was used for the navigation system. The terminal unit could connect with a wide-area ubiquitous wireless network through a wireless gateway [40]. Although the data are