Ozone Sensor and Sampler

Yasuko Yamada Maruo† *and Tatsuya Kunioka*

Abstract

The Environmental Information Systems Project of NTT Energy and Environment Systems Laboratories involves research and development on systems for sensing atmospheric pollutants using chemical sensors. This article introduces a newly developed sensor and sampler for ozone, which is recognized as "the atmospheric pollutant of the 21st century" among various pollutants.

1. Introduction

Ozone is a serious health concern in the USA because it can damage the human respiratory system. Environmental standards for it have been established. The U.S. Environmental Protection Agency (EPA) monitors ozone concentrations throughout the USA and discloses its levels and status on their Web page [1], warning residents in local areas of the potential health risk. In Japan, the government and people have become more and more aware of and concerned about ozone, although they are not as serious about it as Americans. The National Institute for Environmental Studies of Japan regards the 21st century as the century of photochemical oxidants, with the main component being ozone. To enable low-level ozone concentrations in living and working environments to be monitored, we have developed a novel ozone chemical sensor and sampler with extremely high sensitivity and a simple mechanism.

Ozone has a good or bad effect depending on its location. In the stratosphere at heights of more than 10 km above the earth's surface, the ozone layer blocks ultraviolet (UV) light from the sun reaching the earth's surface. This is very important because UV light can harm people, causing problems such as skin cancer and cataracts. However, the ozone layer is being damaged by chlorofluorocarbon gases, and an "ozone hole" through which UV light can pass has formed. On the other hand, the ozone below the stratosphere (i.e., in the troposphere), which is called "ground-level ozone", constitutes a large percentage of photochemical oxidants and is a harmful atmospheric pollutant for humans and vegetation.

Figure 1 shows the yearly change in relative concentrations of atmospheric pollutants up to 2002 and the success rates at meeting the environmental standards in 2002. Although carbon monoxide and sulfur dioxide, which are relatively easy to take countermeasures against, have been declining, photochemical oxidants generated by photochemical reactions related to other atmospheric pollutants like nitrogen dioxide have been steadily rising. Furthermore, the achievement rate for meeting the environmental standard for photochemical oxidants was only 0.3% in 2002, and the areas where photochemical oxidant warning are issued continue to spread around the metropolitan areas year by year. In the Kanto region, the affected area has extended over Saitama and Gunma prefectures to Yamanashi prefecture.

One of hazardous effects of ozone on human health is damage to the respiratory system when it is inhaled. The U.S. EPA reports that long-term exposure to ozone can be a health hazard even if the exposure level is low and that ozone can also reduce agricultural harvests by damaging the leaves of crops.

In various industries, ozone has been used because of its strong oxidizing and sterilizing properties. Examples include the sterilization of food, running water, food-processing factories, and swimming pools; deodorization of toilets, livestock barns, and office spaces; processing of sewage; and cleaning of

† NTT Energy and Environment Systems Laboratories
Atsugi-shi, 243-0198 Japan
E-mail: Maruo@aecl.ntt.co.jp

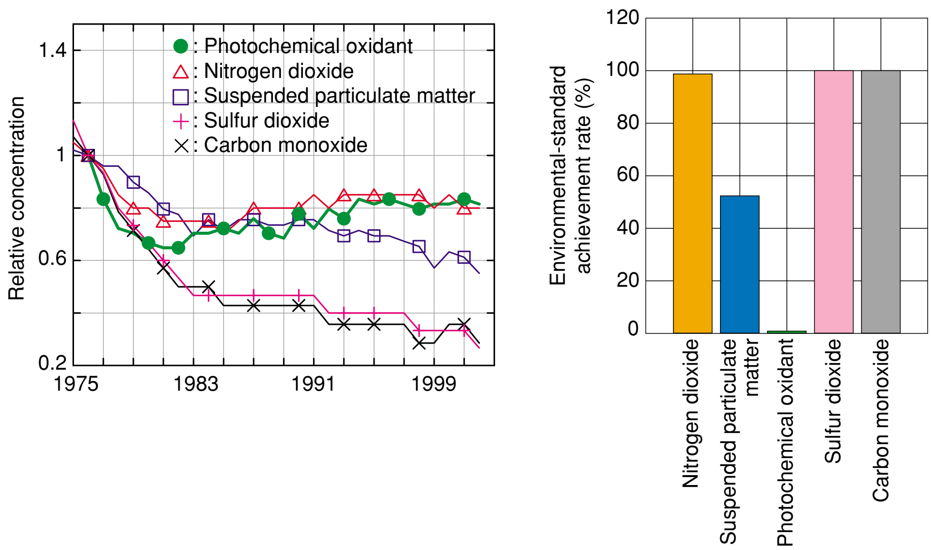

Fig. 1. Yearly change in atmospheric pollutants and environmental-standard achievement rate in 2002.

electronic components like printed circuit boards. Since ozone can be easily generated artificially and it is decomposed into oxygen without any harmful byproducts after use, ozone has become a major sterilizer with an expected annual increase in industrial consumption of 6.3%. An allowable concentration in working places of 100 ppb has been set up.

2. Existing ozone measuring methods

Two methods for measuring such low concentrations of ozone in the atmosphere are prescribed in the Japanese Industrial Standards (JIS) [2]. The first one utilizes a chemical reaction in a neutral aqueous solution of potassium iodide, where the iodide anion is generated in the reaction with oxidants and is quantitatively analyzed by the photo-absorption method. The other one measures the characteristic UV absorption of ozone itself. These methods enable us to measure the ozone concentration with high sensitivity and accuracy, but the equipment required for them is large and not easy to operate. Consequently, it is very difficult to apply these methods to personal monitoring of ozone exposure.

To measure personal ozone exposure doses, the passive sampling method has been used. In this method, the target gas (ozone in this case) is collected in an absorbent fluid sampler. This simple sampler is portable and easy to use, but the collected ozone must then be analyzed with a large instrument like an ion chromatograph, which involves complicated procedures. Therefore, personal monitoring of ozone cannot be done easily in a short period of time with this method.

3. New method to measure ozone concentration and personal exposure doses

NTT Energy and Environment Systems Laboratories recently developed a novel sensor for nitrogen dioxide (NO_2), using a coloring reaction. It uses a porous glass with a vast number of nano-pores, which looks transparent and contains a specific reactive coloring dye in the nano-pores. With its huge effective surface area, this sensor can detect an extremely low concentration of NO_2, such as the level in the atmosphere. We extended this technique to ozone sensing and found that a specific dye in the nano-pores loses its color when it reacts with ozone. The discoloring behavior of this ozone-sensing glass plate with ozone exposure is shown in **Fig. 2**. The huge surface area of the glass enables us to recognize discoloration caused by an extremely low concentration of ozone in the atmosphere. This discoloration reaction is irreversible, so the glass does not regain its color. The degree of discoloration is a function of the total amount of ozone that has been in contact with the glass, which can be easily evaluated by visually inspecting the sensor's glass plate, as shown in Fig. 2. The glass plate is small and lightweight, so it can be incorporated into a compact badge and used to evaluate an individual's ozone exposure in a working environment.

Since the nano-porous glass plate is transparent, the

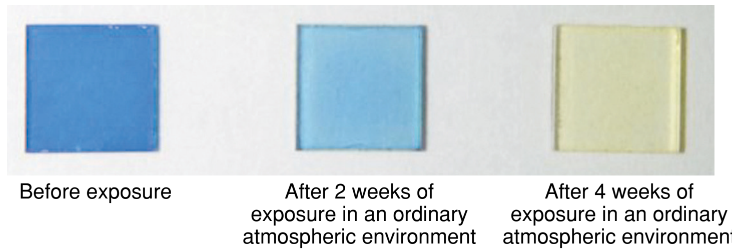

Fig. 2. Discoloration of sensor element.

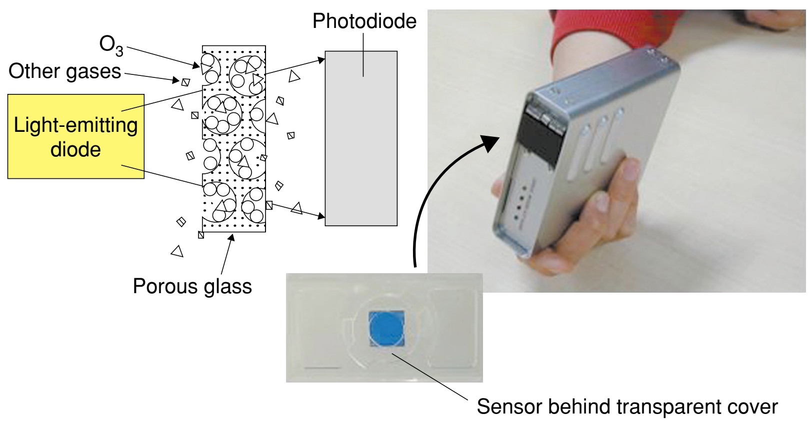

Fig. 3. Principle of sensor element and external view of sensor element and device.

ozone concentration can be more accurately evaluated by comparing transmittances before and after exposure to ozone. For this measurement, we have developed a compact device, 20 cm × 10 cm × 8 cm in size, that uses a small light source (light-emitting diode) and photodetector (**Fig. 3**). The sensor element of the glass plate is inserted under a cover and air is introduced to the sensor element through slits in the side panels. The ozone in the introduced air reacts with the dye incorporated into the sensor element. The device has a timer so that the transmittance of the sensor element is measured for a predetermined time. The results are stored in the device's onboard memory and can be either downloaded to a personal computer or transmitted in real time through wireless and/or other networks. The device also has sensors for recording the temperature and humidity together with a time stamp. The transmittance values are converted into ozone concentrations, which can be plotted against time, and the data series for each monitoring site can be compared with those for other sites. Since the sensor element must be replaced after an exposure exceeds its full capacity, e.g., a month in an ordinary atmospheric environment, the device also includes a function for sending a replacement warning message via the communication network.

4. Ozone sampler with higher sensitivity

With the use of ozone rising in industrial fields, an occupational-health safety standard for people using ozone in the work place has been set up. The exposure level is 100 ppb × 8 hours and the daily ozone exposure must be less than this. Since the glass sensor element made of porous glass described in Section 3 is designed to monitor ozone over a longer period of time, it is not suitable for this application, which requires higher sensitivity. To meet this requirement, the evaluation of the daily exposure dose of individual workers, we have increased the sensitivity by introducing paper as a host matrix medium. Since paper is a porous material, high sensitivity can be expected and the sensor should be cheap and more suited to mass production. However, paper is not transparent, so transmittance measurement is not possible. Nevertheless, the color change of the developed ozone-detection paper after the equivalent of one day of ozone exposure can be visually recognized due to the improved sensitivity. Accordingly, we devised and made an ozone sampler in which the ozone-

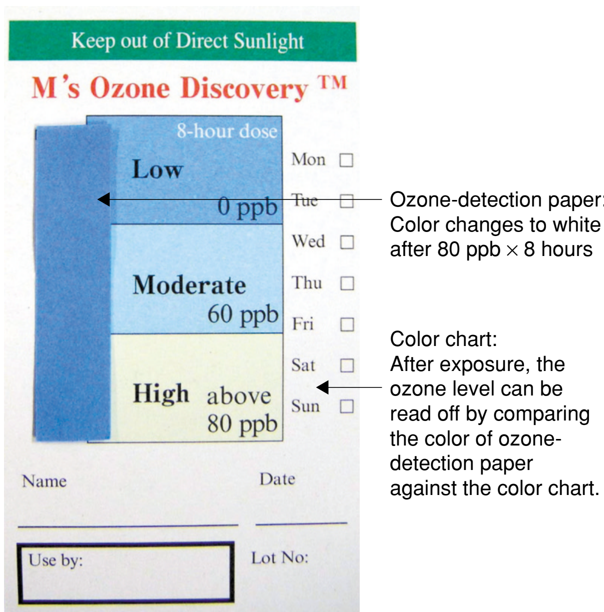

Fig. 4. Ozone sampler.

detection paper is set on a substrate paper sheet with a standard color chart (**Fig. 4**).

The ozone-detection paper is blue before exposure to ozone and gradually loses the blue color with increasing ozone exposure. After eight hours of exposure, the color is compared with the color standards, which correspond to three exposure levels. If the color after exposure matches the "high" color on the chart, the ozone exposure was more than 80% of the exposure limit. In that case, some improvements in the working environment need to be implemented. On the other hand, if some blueness remains after eight hours of exposure, the working environment is considered to be within the exposure limit, indicating a satisfactory degree of safety. Since this method involves accumulative sensing, it may not properly evaluate exposure to a high concentration of ozone within a short period of time. In cases where that is a risk, another method, such as odor assessment, should be combined with this method.

We believe that this readily portable ozone sampler is the most suitable choice for the evaluation and management of personal ozone exposure in working environments.

5. Future development

Ozone is likely to be used more and more in industrial fields, even though concern about it among the atmospheric pollutants will increase in environmental quality management. We will continue to promote the ozone sensor and sampler commercially and reflect the feedback from customers in our research and development so that we can put better products on the market. In addition, we will extend our research to other hazardous pollutants to better meet the demands of the market.

References

[1] http://www.epa.gov/epahome/ozone.htm
[2] JIS B 7957

Yasuko Yamada Maruo

Senior Research Engineer, Environmental Information Systems Project, NTT Energy and Environment Systems Laboratories.

She received the B.E., M.S., and Ph.D. degrees in chemistry from Tohoku University, Miyagi in 1984, 1986, and 2003, respectively. She joined NTT Electrical Communication Laboratories, Tokyo in 1986 and engaged in research on surface characterization using synchrotron radiation and on polyimide materials for optical devices. She is currently engaged in research on chemical sensors for the atmospheric environment. She is a member of the Japan Society of Applied Physics (JSAP), the Japan Society for Atmospheric Environment, and the Japan Radioisotope Association.

Tatsuya Kunioka

Senior Research Engineer, Supervisor, Environmental Information Systems Project, NTT Energy and Environmental Systems Laboratories.

He received the B.E. and M.E. degrees in electrical engineering from Waseda University, Tokyo in 1985 and 1987, respectively. He joined NTT LSI Laboratories, Kanagawa in 1987. He is a member of JSAP and the Society of Instrument and Control Engineers.