

Monitoring of Ambient Ozone: Instrumentations and Applications

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This short review provides the recent progresses on continuous monitoring of atmospheric ozone. The analytical performance is defined in US-EPA 40 CFR Part 53, and Federal Equivalent Method for ozone adopts an ultraviolet photometry to meet the definition. Chemical monitoring systems including spectrophotometry with dye bleaching, chemiluminescence, and bioluminescence have been developed to satisfy the analytical performance. Changes in the electric resistance of semiconductors are also utilized for the measurements. Some of the proposed instruments have been applied to the monitoring of ozone in the ambient air, and reliable results are demonstrated.

Keywords Ambient ozone, monitoring instruments, UV photometry, spectrophotometry with dye bleaching, chemiluminescence, electric resistance

1. Introduction

In the stratosphere, ozone is generated by the photolysis of oxygen molecule by UV light, and the ozone in the stratosphere is beneficial to animals, plants, and organisms. The presence of the ozone layer protects us from the exposure to strong UV ray. On the other hand, the chemical property of ozone of strong oxidant is harmful in the troposphere. When a human is exposed to ozone, the lung function would be impaired. Ozone is mainly generated by photochemical reactions from NO₂ involving the reaction with nitrogen oxides and volatile organic compounds. It is reported that the ozone production is increasing in the troposphere by the rapid population growth and industrialization, especially in Asia [1]. Therefore, continuous monitoring of ambient ozone is a very important task, and demands on the monitoring is growing. In 2015, US Environmental Protection Agency (US-EPA) revised the ozone standards; the primary and secondary ozone standard levels to 0.070 parts per million [2,3]. The performance criteria of the monitoring are defined in US-EPA 40 CFR Part 53 [2]. In the criteria, the performance parameters are defined on 1. Range, 2. Noise, 3. Lower detectable limit, 4. Interference equivalent, 5. Zero drift, 6. Span drift, 7. Lag time, 8. Rise time, 9. Fall time, and 10. Precision. Ozone in the ambient air would be monitored satisfying such performance parameters.

In this short review, some monitoring systems for ambient ozone are introduced. The sensing system based on chemical reactions adopted are spectrophotometry with dye bleaching, chemiluminescence, and bioluminescence. Changes in the electric resistance of semiconductors by its oxidation are also

utilized. Practical ozone monitoring in the ambient air are demonstrated by the proposed instruments, and reliable results are reported.

2. Monitoring by commercial UV photometers

In USA, Federal Equivalent Method (FEM) for ozone uses an ultraviolet photometry [2], and the performance criteria are defined in US-EPA 40 CFR Part 53 [2]. Two commercial instruments based on UV photometry, certified as an FEM by the U.S. EPA (2011), have been tested for the monitoring of ambient air ozone [4]. A chemiluminescence instrument was also tested [4]. The data of 8-h average was consecutively corrected for 3 months, and the number of the days exceeding the standard level (60, 70 or 75 ppb) have been compared. Higher ozone average was occasionally measured by the conventional UV photometer, and the deviation of the instrument was attributed to positive interferences with volatile organic compounds.

3. Monitoring by spectrophotometry with dye bleaching

Ozone is one of the strong oxidant, and many dyes can be bleached by the reaction with ozone. Indigo analogues are a series of popular dyes used for the determination of ambient ozone by bleaching, and the degree of the color fading have been used for the determination.

Tubular gas permeation device was designed for the continuous contact of ambient air with a dye solution of indigotrisulfonate (ITS) [5]. The ozone in the ambient air permeates the porous polypropylene tube, and it bleaches the ITS. The porous tube itself is also a long path-length (5 cm)

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photometric detector. The residual concentration of ITS dye was monitored at 595 nm by an LED-PD detector. Although the ITS dye is bleached by the reaction with ozone, the ITS dye can be concentrated by the evaporation of the solvent through the porous tube. Degree of the evaporation depends on the relative humidity of the air, and the stability of the background absorbance should be assured even at the different humidity and the solvent evaporation. The effect of the evaporation-concentration of the ITS dye was corrected with a stable dye of food yellow No. 5 (FY5) monitored at different detection wavelength at 460 nm by an LED-PD detector. The FY5 was also concentrated by the evaporation in the same degree, and the change in the absorbance at 460 nm was used for the correction of the absorbance at 595 nm. The limit of detection for ozone was 1.2 ppbv, and a linear span up to 300 ppbv was obtained at a sampling time of 1 min. Continuous monitoring of ambient ozone was also demonstrated for more than 10 days [5].

The bleaching of the dyes for the monitoring of ozone was utilized in the film and paper. Indigo carmine was retained on a transparent porous glass chip (8 mm × 8 mm square and 1 mm thick, average pore diameter of 4 nm, and a specific surface area of 200 mm²/g) [6]. After immersing and drying the glass plate, the chip was exposed to a gas flow in a glass chamber for a certain period. The indigo carmine was degraded by the exposure to ozone, and decrease in the absorbance at 611 nm was measured by an LED-PD photometric detection. Therefore, the ozone amount determined by this device is the accumulated amount. The calibration graph was linear in the concentration range of several tens of ppb, and the detection limit for ozone was about 3 ppb for a 1 h exposure [6].

Indigo carmine was also supported on a filter paper [7]. A cellulose filter (20 mm × 20 mm square, 0.26 mm thick, and a density of 125 g/m²) was immersed in a reagent solution containing indigo carmine, citric acid, and glycerol and dried. The sheet was placed on a plastic plate in a chamber, and ambient air was flown in the chamber at 1.5 m/s. The reflectance was measured by a spectrophotometer or by an LED-PD photometer. Logarithmic value of reflectance⁻¹ at 618 nm was linear with accumulated ozone concentration up to 400 ppb×h. Ambient ozone was continuously monitored every 1 h by an LED-PD detector at 611 nm. The hourly averaged ozone concentration agreed well with the results of a commercial analyzer in a ±5 ppb error range [7]. Azo dyes of Orange I and Orange II were also used instead of indigo carmine [8]. The bleaching by the ozone exposure was intense with Orange I at alkaline conditions of pH > 11. Hydroxyl group of Orange I at

the para position was attributed to the sensitive detection of ozone [8]. No interference was observed with some oxidized gases, while indigo carmine was interfered with H₂O₂ [7].

Indigotrisulfonate dye was retained on a cellulose filter, and the filter was set in a passive sampler [9]. After 8-h exposure to the ambient ozone, the deepness of the color was compared with the color standards prepared with standard ozone; the color standards were reproduced as printable digital images. The color standard covered the ozone amount from 5.25×10⁻⁹ mol to 1.58×10⁻⁷ mol. Spectrophotometric and visual techniques were used for the determination of the ambient ozone, and ozone concentrations were determined in the concentration range from 9 to 55 ppbv [9].

4. Monitoring by chemiluminescence

Chemiluminescence (CL) performs sensitive detection, and ethylene-ozone chemiluminescence is adopted in the US-EPA reference method [2]. Other CL reagents have been investigated for the sensitive monitoring of ozone, including luminol, Rhodamine B, Eosin Y, and Coumarin 47. Although the CL reagents were usually retained on a solid support such as silica gel, the response was affected by the relative humidity. Liquid-phase CL reagent was thus developed to overcome the effect of the relative humidity.

Chromotropic acid (CA) was found to be a highly sensitive CL reagent for ozone [10]. The CA solution was flown through on top of the detection window of a photomultiplier tube and the air-liquid contact area was continuously refreshed, where the CA solution was exposed to the ambient air and CL was detected. The CL intensity was increased by ~100 times by photo-radiation to the CA solution. The CA was stably activated by a UV-light radiation while flowing through a Teflon tubing at alkaline pH. The response was fast with 130 ms in rise time and 80 ms in fall time, and the calibration range was up to 230 ppbv with a limit of detection as low as 40 pptv. It has been suggested that the primary CL-active species are likely dimeric semiquinone species derived from CA by a series of radical reactions. The monitoring system was applied to the continuous monitoring of ambient air [10].

Another liquid-phase monitoring system was also developed with a liquid film flowing down on a smooth surface of a glass plate (80 mm × 6 mm) [11]. Solution of chemiluminescence reagent was fed on a glass plate through a PTFE tube at a flow rate of 53 μL min⁻¹. Several reagents were examined, and azine dyes of phenosafranin, methylene blue, and safranin O showed the highest detector signals. It was necessary to take 1

h to get stable CL response. Afterward, stable and quantitative measurements were possible in a period of a few days. A linear calibration graph was obtained for 0–300 $\mu\text{g m}^{-3}$ ozone with a limit of quantification of 2.1 $\mu\text{g m}^{-3}$ (0.9 ppbv) [11].

A dry-CL sensor disc was designed for the fast ozone measurement (1–50 Hz) [12]. The dye-coated sensor disc was prepared with Coumarin 47 as a CL reagent, gallic acid as an energy transfer reagent, and Rotisilon A as a diffusion solvent, where thin layer chromatography plates made of silica was used as a disc matrix. It was found that a short time adsorption of 10 s immersion of the disk to the reagent solution lead smaller standard deviations. The preparation method was called as efficient adsorption method (EAM). Additionally, preozonization of the sensor disk for 5 h ensured the maximum sensitivity at the start of the measurement and avoided the strong increase in the sensitivity at the start. The sensor disc was applied to the field measurement at 20 Hz, in Rhine Hessen, Germany; the ozone concentration varied in the range between 1 ppb (nighttime) and 61 ppb (daytime) [12]. The sensor discs prepared by EAM also exhibited small deviation of the sensitivity with the ozone dose of up to $\sim 4,000$ ppb \times h.

5. Monitoring by bioluminescence

Luciferase based bioluminescence is a highly sensitive detection system, and the luminescence scheme was applied to the determination of ozone in aqueous solution [13]. Detection reagents of 6-*O*-alkylated and 6-*N*-acetylated luciferins were designed and synthesized. While the reagents themselves do not undergo light emitting process, the reagents were oxidized by ozone to give luciferin and aminoluciferin, respectively; the products emits with luciferase. Ozone in the aqueous solution was thus been determined. The emission intensity reached maximal values within 5 min. The calibration graph was linear in the ozone concentration in the 0–400 nM (0–15 ppb) range, and the detection limit was 1.0×10^{-11} M with 6-*O*-alkylated luciferin. Interference from other oxidants is little, and the selectivity toward ozone is satisfactory. This measurement system was applied to practical environmental samples. After 8 h adsorption into the buffer solution in a mouth glass bottle, the ozone concentration was determined. The result agreed well with iodometry titration and UV spectroscopy [13].

6. Ozone sensing by electric resistance

Tungsten trioxide sensing film was deposited by sputtering between screen-printed gold electrodes on a 2 mm \times 2 mm

alumina substrate [14]. The electric resistance of the circuit increased by the exposure to ozone. Although high temperature of ~ 530 °C was necessary to get the response, ozone was determined at the concentrations of several tens of ppb [14]. The sensor was applied to the ozone monitoring of urban conditions at Sandwell, UK, and the result agreed well with a UV absorption instrument [14]. When WO_3 sensing film was fabricated onto silicon substrate by sputtering [15], ozone was determined at sub-ppm level [15].

ZnO nanostructures were examined as ozone sensor [16,17]. The sensing mechanism of the sensor was that the electric conductivity was decreased by the oxidation of ZnO nanorods with ozone. The ZnO nanorod was deposited on a glass substrate by aqueous chemical growth at 95 °C [16]. For 5 h growth of the ZnO nanostructure, the nanorods was flowerlike with diameter ranging from 500 to 800 nm and length of ~ 7 –8 μm . When the ZnO nanorods were exposed to ~ 1 ppm ozone, the electric resistance of the ZnO nanorods increased and the electric current decreased by the magnitude of $\sim 10^6$ fold [16]. However, it was necessary to restore the ZnO nanorods by photoreduction directly exposing to the UV light of a mercury pencil lamp in vacuum for 15 min. It was not certain if this sensor is applicable to much lower concentrations of ozone.

The ZnO nanorods was grown by chemical vapor deposition on an alumina plate at 440–600 °C for 10 min, and it was also used as an ozone sensor [17]. The ZnO showed a rapid response time of 45 s and recovery time of 5 s. Calibration graphs were drawn at the ozone concentration range from 1 ppm to 2.5 ppm. Sensor responses of NO_2 , NO and CH_4 are about 1/1000 to ozone, and this sensor is selective to ozone.

7. Summary and prospects

Upon increasing demand on monitoring of ambient ozone, various sensing methods have been proposed. Every methods possess characteristics on monitoring to meet the performance parameters. Some of the monitoring systems proposed were applied to the monitoring of ambient ozone, and reliable results were demonstrated.

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