



A porous glass-based ozone sensing chip impregnated with potassium iodide and α -cyclodextrin



Katsuyuki Izumi^{a,*}, Masahiro Utiyama^b, Yasuko Y. Maruo^c

^a Faculty of Sciences and Engineering, Toyo University, 2100 Kujirai, Kawagoe City, Saitama 350-8585, Japan

^b National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba City, Ibaraki 305-0053, Japan

^c Faculty of Engineering, Tohoku Institute of Technology, Yagiyama, Taihaku-Ku, Sendai City, Miyagi 982-8577, Japan

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ABSTRACT

A chemical sensing chip for gaseous ozone (O_3) has been fabricated by impregnating a porous glass sheet (8 mm square and 1 mm thick) with potassium iodide (KI) and α -cyclodextrin. The latter suppresses volatilization of iodine formed by the reaction of KI with O_3 . When passively exposed to air containing a sub-ppm level of O_3 at a relative humidity (RH) of 90%, this chip changes from colorless to pale yellow, with an absorption peak at 360 nm. A plot of change in absorbance at this wavelength against the total O_3 exposure yields a good linear relationship passing through the origin. From the slope of the plot, the detection limit is estimated to be several ppb, assuming an exposure interval of 1 h. Upon exposure at lower RH values of 50–70%, the chip turns reddish brown and absorbs over the range of 420 to 550 nm, although its absorption maximum remains at 360 nm. Absorption in the visible region under these conditions was found to be transient and thus unsuitable for measuring O_3 , although this visible absorption could be readily shifted to 360 nm by applying higher RH values, such as 90%. From these results, it is concluded that hourly variations of ambient O_3 concentration can be measured by observing the absorbance of the chip at 360 nm, in conjunction with conditioning of the chip at 90% RH following the exposure interval.

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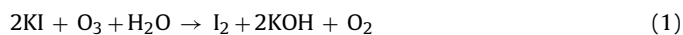
1. Introduction

Ozone (O_3) is an abundant and ubiquitous ground-level air pollutant and is also a major component of photochemical smog. Because of its potential to cause harm to both humans and the ecosystem, O_3 is one of the most important priority pollutants [1]. For several decades, measurements of ambient O_3 have been made at fixed points designated by air quality monitoring networks. Despite its adverse effects, O_3 is also widely applied in various industrial processes, such as bleaching, disinfection and waste water treatment. Thus, the development of simple, easy O_3 measurement techniques is currently an important topic [2,3] in these industries as well as among environmental scientists.

Several methods have been proposed for the measurement of ambient O_3 . These include UV photometry based on strong absorption at 254 nm [1,4], chemiluminescence [1,5], fluorometry

employing O_3 reaction products [6,7], colorimetry based on the fading of a dye [8–14] or the formation of colored reaction products [15–17], semiconducting metal oxide sensors [2,18–27], phthalocyanine chemoresistors [28,29], neutral buffered potassium iodide (NBKI) [30] and electrochemical techniques [18]. Among these, analyzers based on UV photometry are the most reliable and thus are widely employed. However, these techniques are less than ideal when the goal is to perform simultaneous measurements at multiple locations and are unsuited to field observations at sites where power sources are unavailable. To address these shortcomings, less costly sensing devices have recently been introduced to air quality monitoring networks [20,27,31] and more cost-effective passive samplers [9,11,13,14] have been developed on the basis of dye fading colorimetry for use in outdoor locations such as forests.

The working principle of the NBKI method is well established [1]. Here, the concentration of O_3 is determined through the measurement of iodine (I_2) produced by the oxidation of KI (Reaction (1)) in an aqueous solution at a pH of approximately 7.



* Corresponding author at: Department of Applied Chemistry, Faculty of Sciences and Engineering, Toyo University, 2100 Kujirai, Kawagoe City, Saitama 350 8585, Japan

E-mail address: izumi@toyo.jp (K. Izumi).

The iodine in Reaction (1) further reacts with an unreacted iodide ion to form a triiodide ion, as shown in Reaction (2).



Tracking the absorbance of the triiodide ions at 360 nm thus allows the determination of O_3 . In this system, iodine in the liquid phase is in equilibrium with iodine that enters the gas phase through evaporation [32]. This leads to a loss of iodine, and this problem must be minimized in those devices actually used for O_3 measurements based on the NBKI method. In spite of this difficulty, other measurement techniques based on the determination of iodine have also been developed [15,16,33], employing ingenious methods to mitigate the problem of iodine loss. In our own work, we have sought to address iodine loss by employing α -cyclodextrin (α -CD), a non-reducing cyclic oligosaccharide composed of six glucose units (approximate molecular diameter of 1.2 nm and length of 0.6 nm with a cavity diameter of 0.6 nm), based on the formation of a clathrate complex with iodine [34]. The formation of this complex is anticipated to reduce the volatility of iodine and thus suppress iodine losses. In fact, Neoh et al. [35] have shown that α -CD is an effective agent for preventing evaporative losses of iodine from aqueous solutions. Furthermore, Minns and Khan [36] have reported that triiodide ions in aqueous solution react with α -CD to form stable clathrate complexes with strong absorption at 360 nm, and that the intensity of this absorption is two to three times that of free triiodide ions.

A unique aspect of the present study is the use of porous glass (PG) as a substrate for sensing chips. It has been demonstrated that PG-based colorimetric sensing elements impregnated with reagents are sensitive to pollutant gases such as O_3 , NO_2 and formaldehyde, with detection limits in the ppb range upon passive exposure over several hours [10,37–39]. Passive sensing has advantages, such as ease of use and the absence of a requirement for a sampling protocol and a power source, although this method typically generates slower responses. The characteristics of PG have been described in detail elsewhere [40]. Briefly, this material has a high specific surface area, uniform pores with a narrow pore size distribution, and transparency to light over a wide range from near UV to near IR. The former two characteristics favor the adsorption of pollutant gases on the PG surface. Because PG-based colorimetric sensing elements are highly sensitive, we believed that a sensitive O_3 detection chip could be fabricated by impregnating PG with a combination of KI and α -CD.

In this study, we produced an O_3 sensing chip based on the above concept and report herein preliminary results regarding the performance of PG-based sensing chips prepared by immersing small sheets of PG in an aqueous solution of KI and α -CD.

2. Material and methods

2.1. Materials

A sheet of Vycor 7930 PG (1 mm thick, Corning Inc.) cut into 8 mm squares was used as a substrate for the chips. The Vycor glass had a specific surface area of $200 \text{ m}^2/\text{g}$ and contained numerous pores with a narrow size distribution and an average pore diameter of 4 nm and a pore volume of 28%. Prior to use, the glass was washed successively with methanol, acetone and ultrapure water (specific resistance of $18.3 \text{ M}\Omega \text{ cm}^{-1}$). This same water was used in all of the experimental work carried out in this study. Both a twentyfold-concentrated phosphate buffer solution and KI were purchased from the Kanto Chemical Co., Inc., while α -CD was obtained from Hayashibara Biochemical Laboratories, Inc. and used without purification.

2.2. Preparation of sensing chips

The cleaned glass sheets were immersed for 3 h in a phosphate buffer solution (pH 7.0) containing 0.043 M α -CD and 0.05 M KI and then held in O_3 -free air for 1 h. The PG sheets prepared in this manner were subsequently used as the sensing chips. A preliminary test to ascertain the stability of the chips found no formation of iodine as assessed by following UV absorption at 360 nm (Shimadzu, UV-1650PC) during storage over one day. Between trials, all chips were stored in plastic bags laminated with aluminum.

2.3. Ozone exposure experiments

Fig. 1(a) shows the apparatus used to perform O_3 exposure trials. A portable UV–vis spectrometer (Ocean Optics, USB4000) with fiber optic cables was employed to obtain *in situ* absorption spectra. The sensing chip was fixed in a 2 mm deep groove within a small polyethylene stand that was situated at the base of a filter holder (Ocean Optics, FHS-UV), so as to position the specimen within the light beam from the optical fiber cable. A photographic image of the filter holder ($4 \times 3 \times 2.8 \text{ cm}$) on which the chip was mounted is presented in Fig. 1(b). The distance between the set screw at the left side and the wall of the filter holder was approximately 5 mm and the chip was positioned vertically in the center of the unit so that O_3 was able to reach the chip from both sides. The filter holder containing the chip was subsequently inserted in a cylindrical glass chamber (5 L in volume, $15 \times 29 \text{ cm}$) to allow exposure to air containing O_3 at $20\text{--}22^\circ\text{C}$ and a relative humidity of 50% or more. Absorption spectra were acquired at 1 min intervals during the exposure. A glass optical filter (Schott, KG3, 1 mm thick) that transmits wavelengths between 320 and 750 nm was positioned between the light sources (D_2 and tungsten lamps) and the filter holder to suppress iodine formation in the chip due to UV or IR irradiation by the lamps. Laboratory air was purified for use in this study by passing it through silica gel and activated carbon. Water vapor was added to the base air by flowing the air over the surface of ultrapure water contained in flasks. An O_3 generator (DKK OZ-200) based on the pulse irradiation of air with a Xenon lamp supplied O_3 to the chamber. The concentration of O_3 was monitored by an ultraviolet absorption analyzer (DKK GUX-213J). To maintain a uniform concentration of O_3 and humidity in the test chamber, the air inside the chamber was constantly mixed at a slow rate using a small fan. The filter holder was carefully positioned such that the chip was leeward with respect to the direction of air flow from the fan. Humidified air containing O_3 was supplied to the test chamber at a rate of approximately 2 L/min. The UV absorption-based ozone analyzer drew the air out at a rate of 1.5 L/min, while a sensor (SATO thermo- and hygrometer) passively monitored the temperature and humidity. The residual air (0.5 L/min) was expelled through a vent. Typically, both the humidity and the concentration of O_3 in the chamber reached steady values following an interval of 15 to 20 min.

3. Results and discussion

3.1. Ozone exposure at high humidity

Prior to the main trials, chips prepared without any α -CD were exposed to O_3 for comparison. Typical spectral changes observed during such exposures are shown in Fig. 2 as a function of time. In the trial pictured, the O_3 concentration was approximately 0.15 ppm and the RH was about 90%. A single absorption peak is observed at 360 nm, similar to that observed in the absorption spectrum of an aqueous solution containing iodine and KI. Previously, Minns and Khan [36] reported that the peak at 360 nm can be

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