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Article

Colorimetric Determination of Ambient Ozone using Indigo Blue Droplet

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Um método simples e sensível, baseado em uma gota líquida, é descrito para medida do ozônio atmosférico. Uma gota de 30 μL de solução de índigo azul é suspensa em uma corrente de ar para amostragem. O ozônio coletado reage com a solução de índigo azul, provocando seu descoramento. O sensor colorimétrico é composto por duas fibras ópticas; a fonte de luz monocromática usada foi um LED vermelho (625 nm). A curva analítica foi construída com concentrações padrão de ozônio, na faixa de 37 a 123 ppbv. O limite de detecção alcançado foi 7,3 ppbv. O método considerado mostrou-se de fácil aplicação e resposta rápida, com um tempo total de análise de apenas 5 minutos.

A simple and sensitive method based on a liquid droplet is described for the measurement of atmospheric ozone. A 30 μL drop of indigo blue solution is suspended in a flowing-air sampling stream. The ozone collected reacts with the indigo solution resulting in its decolorization. The colorimetric sensor is composed of two optical fibers and the source of monochromatic light was a red LED (625 nm). The calibration curve was constructed with ozone standard concentrations ranging from 37 - 123 ppbv. The detection limit achieved was 7.3 ppbv. The method considered here showed itself to be easy to apply with a fast response and a total analysis time of only 5 minutes.

Keywords: ozone, colorimetric sensor, optical fibers, liquid droplet

Introduction

Ambient ozone, produced during NO_2 photolysis at wavelengths < 400 nm, is a common urban and regional air pollution problem in many parts of the world.[1-3] Photolysis of ozone at wavelengths < 319 nm is important as the main source of hydroxyl radical (OH), which largely determines the oxidative capacity of the lower atmosphere.[4-7] When present at high concentrations ozone can cause a range of adverse environmental impacts on human health, crops, natural vegetation and outdoor materials.[8-12] Concentrations of background ozone appear to have been increasing since the industrial revolution. In outdoor ambient air, the increase is often due to increased road transport emissions of precursor compounds,[2] while indoors (e.g. in offices) it may be due to use of laser printers and photocopiers.[13,14]

The monitoring of ambient ozone is an essential first step in understanding the processes and mechanisms of the formation of ozone.[15] The need for analytical methods to determine ozone has therefore assumed considerable importance.

Published methods for the determination of ozone involve a variety of indirect wet and direct instrumental analytical methods. Many of the earlier wet analytical methods have not been utilized in recent years. In particular, colorimetric methods nowadays have received little application to atmospheric ozone, because most of them have inadequate sensitivity.[16] Ultraviolet light and chemiluminescent analyzers have been applied successfully to measure low concentrations of ozone at urban and non-urban sampling locations.[17] Although these methods allow determination of ozone concentrations in real time, they utilize large, heavy and expensive instruments. Obviously a simple and specific method to analyze ozone, which combines low cost, fast response and light weight can have wide application for the monitoring of ambient ozone.

The principal limitation in developing an analytical method for ozone is its high reactivity. Ozone cannot be collected and preserved, and it is generally assumed that ozone decomposition is catalyzed by surface contact.[12] For the sampling system, glass or Teflon should be used and the ozone should have minimal contact with any other surface. With the exception of electrochemical, direct optical spectroscopic or UV absorption techniques,

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methods employed to estimate atmospheric ozone have two stages, the first of which is the reaction of ozone with a specific reagent and fixation and storage of the product in a suitable medium. Next, the indirect determination of the product is undertaken using a convenient technique. However most of these methods possess inadequate sensitivity and involve laborious procedures of sample preparation and determination, which increases the possibility of contamination.[18]

In this paper, we report on the analytical use of a droplet-based ozone gas collection and analysis system. The use of droplets coupled with an optical fiber chemical sensor to analyze trace gases *in situ* and without sample manipulation has been developed. This approach has proved promising for determination of several gases.[19-22] A reagent droplet suspended at the tip of a small tube represents a sampling approach that provides a renewable surface, consumes little reagent and gives minimal contact between the gas and the surfaces. The renewable gaseous sample interface is based on the repeated formation of liquid droplets. By flowing a gaseous sample across a reagent droplet, soluble analytes contained in the sample diffuse into the liquid drop. The detection of the analyte is achieved by coupling the reagent solution droplet with a fiber-optic/light emitting diode (FO/LED), which measures changes in any optical property due to the analytical reaction.

The design and characteristics of a light-emitting diode (LED) based system are demonstrated using the colorimetric determination of ozone gas via the indigo blue decolorization reaction. In this reaction, ozone adds itself across the carbon-carbon double bond of the sulfonated indigo dye. The resulting bond cleavage forms colorless products, and the change in absorbance at 600 nm is proportional to the concentration of ozone.[23-24] Advantages of this sampling/sensor system are minimal contact of ozone with surfaces, quick response, selectivity and no sample manipulation.

Experimental

Reagents and standard solutions

Reagent grade chemicals were used throughout this work. Deionized water (18.2 MW cm) produced by a MilliQ System (Millipore, Bedford, MA) was used to prepare all solutions.

Stock solution

An indigo reagent stock solution was prepared by adding 2.50 g of potassium indigo trisulfonate (Aldrich) to a 1 L volumetric flask containing approximately 500 mL of water, 1 mL of concentrated phosphoric acid, and 10 g of sodium dihydrogen phosphate, stirring the mixture, and diluting the solution to 1 L. This solution was stored in the dark, and is stable for at least 4 months.

Working solution

Reagent working solution was prepared by adding 1 mL of indigo reagent stock to a 10 mL volumetric flask and making up to volume with deionized water. The working solution was prepared daily.

Measurement system

The droplet-based measurement system arrangement is shown in Figure 1. A Teflon tube T2 (11 mm i.d., 13 mm o.d. and 35 mm in length) is fixed in a fitting M that is screwed into an opaque tube SC (15 mm i.d., 18 mm o.d. and 65 mm in length), the latter serving as sampler chamber. Indigo blue solution is pumped by a peristaltic pump P (Ismatec, model 7335-50) through the Teflon tube T1 (0.3 mm i.d. and 0.8 mm o.d.), into tube T2. The indigo solution is allowed to flow to form a droplet on the tip of tube T2. The flow rate used was 60 μL min^{-1}. A three-way valve is incorporated in the liquid inlet line and when the valve is shut off, liquid flow stops and the drop volume remains static. A high-intensity red light-emitting diode was used as the light source (625 nm). Although established methods

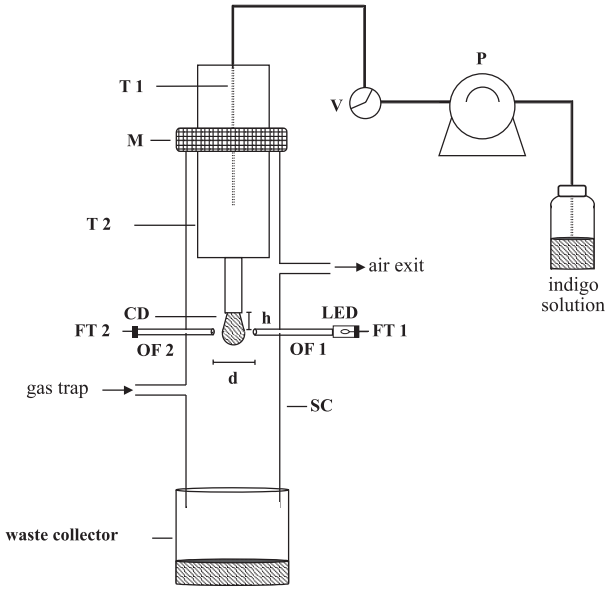

Figure 1. Schematic diagram of the drop based sampling/detection chamber. FT1,2, photodiodes; OF1,2, plastic optical fibers, 1 mm core; CD, droplet collection; SC, sampling chamber; M, fitting; T1, Teflon tube for liquid delivery; T2, Teflon tube for drop formation; V, three-way valve; P, peristaltic pump; *h*, vertical distance between the drop head and the center-line of the optical fibers; *d*, distance between the two optical fibers.

recommend a measurement wavelength of 600 nm, the dye absorbs in a broad spectral region[25] and minimal loss of sensitivity is expected at 625 nm. The beam of light is transported from the LED to the droplet by a plastic optical fiber OF1 (1 mm in diameter). On the diametrically opposite side, the transmitted light is conducted to a silicon photodiode (S2007, Electronic Goldmine, Phoenix, AZ) by another plastic optical fiber OF2 (1 mm in diameter). A reference silicon photodiode is placed at the back plane of the LED to provide a referenced absorbance detection arrangement. The reference and the signal photodetector outputs are processed by a home-built current detector[26] that produces the absorbance output, which is registered by a microcomputer. The sampling chamber was closed inside a box, to prevent interference from outside light during the data acquisition.

Standard gas O_3 generation system

The standard gas O_3 generation system is schematically shown in Figure 2. The source of the carrier gas was an oil-free compressor (model DE, Barionkar, Osasco, SP, Brazil). All gas flows are regulated by mass flow controllers FC 1-5 (Gilmont Instrument, Racine Wi). Air purified by sequential columns A1 (activated carbon), A2 (silica gel) and A3 (potassium iodide) is metered by flow controller FC1. One portion of the pure air flow, controlled by FC2 (0.3 L min^{-1}), was directed through a glass chamber in which a germicidal ultraviolet lamp (4 W) was fixed. The mouth of the chamber was sealed with a cork through which passed the leads of the lamp and an outlet tube. After initial assembly of the ozone-generation apparatus, the lamp was partially covered with aluminum foil to minimize ozone production, and the system was allowed to come to equilibrium for 10 days to allow for any reaction of ozone with the aluminium foil. When the system is operating, ozone concentrations in the sample line are varied by gas dilution and the flow can be regulated such that the desired amount of standard gas flows through the sampling chamber. The excess flow is metered by flowmeter (FC4) and is then aspirated by a suction pump. The ozone concentration was standardized using the iodometric method. This method utilizes the reaction between potassium iodide solution (buffered at pH 6.8 ± 0.2) and ozone, which liberates an equivalent amount of iodine. The liberated iodine is determined by spectrophotometric measurement of the absorbance of triiodide ion.[16]

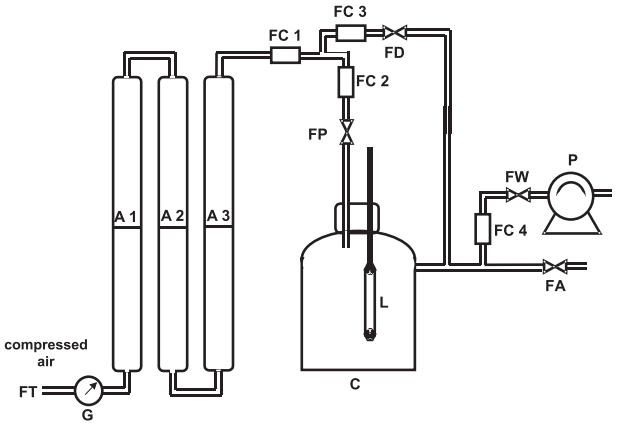

Figure 2. O_3 gas generation system: FT, total flow rate; G, pressure gauge and regulator; A1-3, sequential columns for air purification; FC1-5, mass flowmeters and controllers of total mass, chamber, dilution, waste and sample flow rate; FP, chamber flow rate; FD, dilution flow rate; FS, sampling flow rate; FW, waste flow rate; C, glass chamber; L, germicidal ultraviolet lamp; P, vacuum pump.

Results and Discussion

Geometry of the measuring system

During optimization of the proposed measurement system different geometries were tested in order to achieve the best analytical signal. The position of the optical fibers OF1,2 relative to Teflon tube T2 (expressed by *d* and *h* in Figure 1) determines the manner in which the droplet is probed by the source beam, and thus affects the detection sensitivity. Hence various *h* and *d* values were tested to examine their effects on the measured absorbance. In these tests, deionized water and indigo solution were used. When the optical fibers OF1,2 and the Teflon tube T2 were positioned with *h*= 3.0 mm and *d*= 7.5 mm, the best analytical signal was obtained and the sensor gave the highest difference between the analytical signals measured using water and indigo blue solution. Figure 3 shows the measured absorbance recorded during the lifetimes of three droplets.

The minimums seen in these lines represent the maximum light intensity transmitted between the source (OF1) and the collector (OF2) fibers. The analytical signals do not change rapidly near this minimum, so that the absorbance is not affected by any small droplet change. As the lifetime of the droplet is a direct function of the outflow of the peristaltic pump, it was possible to find that the minimum value of absorbance was observed for a volume close to 30 μL. Therefore, this static volume was adopted in our subsequent experiments.

The analytical response of the measurement system was evaluated for different indigo concentrations (from 0 to 8.1 x 10^{-4} mol L^{-1}) and showed a linear relation between the indigo blue concentrations and absorbance values, described by the equation 1:

$$A = (2.34 \pm 0.32) \times 10^{-2} + (5.68 \pm 0.07) \times 10^{-2} \text{ [indigo]} \quad r = 0.9993 \qquad (1)$$

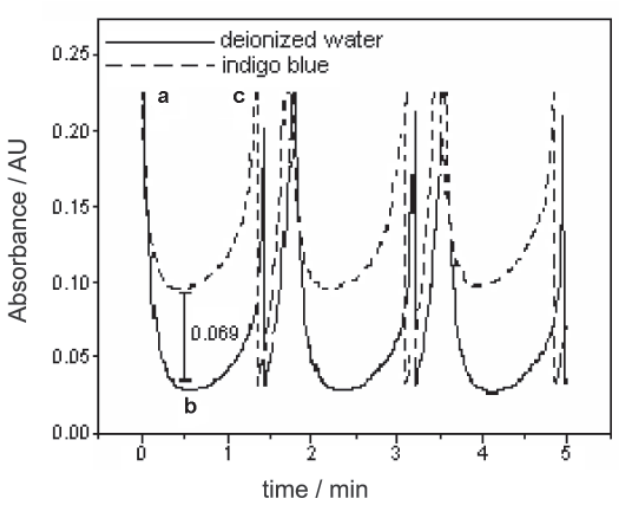

Figure 3. Signals from deionized water drops and drops containing an indigo blue solution with optimized positions of the optical fibers and drop former. Three successive drops are shown in each case. a) beginning of drop formation; b) sampling volume of drop 30 μL; c) drop maximum volume before it falls.

where A represents absorbance and [indigo] the indigo concentration in mol L^{-1}.

Effect of the sampling period

Sampling time is an important parameter to establish. Short times could be insufficient to collect the analyte in an amount necessary for its determination; long times can saturate the collector, decreasing the collection efficiency. Thus, some tests were carried out involving different sampling times. First, measurements were done only with pure air samples (that contained no analyte). Low relative humidity of the sample can indirectly affect the measurements by evaporating the droplet. If the droplet evaporates and there is a concentration of dye within the droplet, then the absorbance will increase. When pure air is sampled at 0.2 L min^{-1}, outside the range of a 13 min period, the increase in absorbance is sufficient to cause an analytical error (Figure 4). In this experiment the sample air humidity was close to zero and the evaporation on the droplet was the greatest possible. A more humid sample will cause less evaporation of the droplet. For longer periods of sampling, the evaporation must be compensated. A second sampling of scrubbed air without ozone can provide this compensation, and the signal difference between air with and without ozone must be considered as the analytical signal. Thus, in the second experiment, sampling was done with 100 ppbv of ozone for times ranging from 1 to 15 min. Next, ozone was scrubbed from the air by using silica chemically impregnated

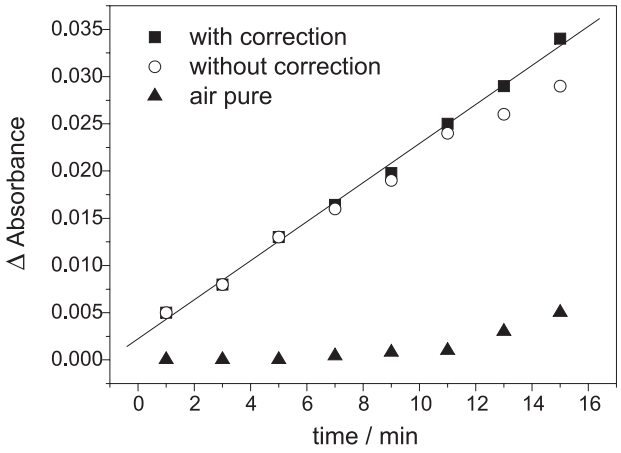

Figure 4. Analytical signals observed as a function of sampling times. Sampling flow rate = 0.2 L min^{-1} and $[O_3]$ = 100 ppbv.

with potassium iodide, and sampling was done for the same range of time. Figure 4 shows the results obtained. Curves fitted to the data points are described by equations 2 (with correction) and 3 (without correction).

$$\Delta A = (2.2 \pm 0.47) \times 10^{-3} + (2.1 \pm 0.051) \times 10^{-3}\ t \quad r = 0.9982 \qquad (2)$$

$$\Delta A = (2.6 \pm 0.75) \times 10^{-3} + (2.1 \pm 0.22) \times 10^{-3}\ t - (2.1 \pm 1.3) \times 10^{-5}\ t^2 \quad r = 0.9955 \qquad (3)$$

where ΔA represents the difference between the analytical signals before and after ozone sampling and t is the sampling time in minutes.

It can be observed that if the difference of signals between the sample containing pure air (without ozone) and the sample containing air with ozone is not considered, a divergence occurs after 13 min of sampling, which causes error in the measurements. Therefore, for longer sampling, it is necessary to subtract the blank absorbance values (air without ozone) from the values of air with ozone.

The measurement protocol reported here involves: (*i*) the formation of a stable droplet (30 μL) and recording the initial baseline absorption; (*ii*) the sampling of ozone at a given concentration and for a fixed time; (*iii*) after sampling has finalized, waiting until the absorbance no longer changes, recording this value and its difference from the initial baseline value, the difference being used as the analytical signal; and (*iv*) forming a new droplet and beginning the sampling again. The time profile of ozone measurements is dependent on the rate at which the reaction occurs (step *iii*). The indigo reaction has the virtue of using a single reagent that contains one double bond, which reacts with ozone with a very high reaction-rate constant (>10^7 mol^{-1} L s^{-1}).[25] Using a 5 min sampling

time, the results showed that there was no significant difference between the absorbance values obtained either immediately after the sampling was finalized, or after a reaction-wait time of 20 min, indicating that it is not necessary to wait a longer time for the reaction to occur as the process is fast.

Effect of the sampling flow rate

The sampling flow rate was another important analytical parameter evaluated. In diffusion-based collection systems, the efficiency of sampling initially increases with increasing sampling rate and then the slope decreases and a virtual plateau is observed at higher flow rates.[27] In this experiment, 100 ppbv ozone was sampled for 5 min, with the sampling flow rate varying from 0.1 L min^{-1} to 0.5 L min^{-1} (Figure 5).

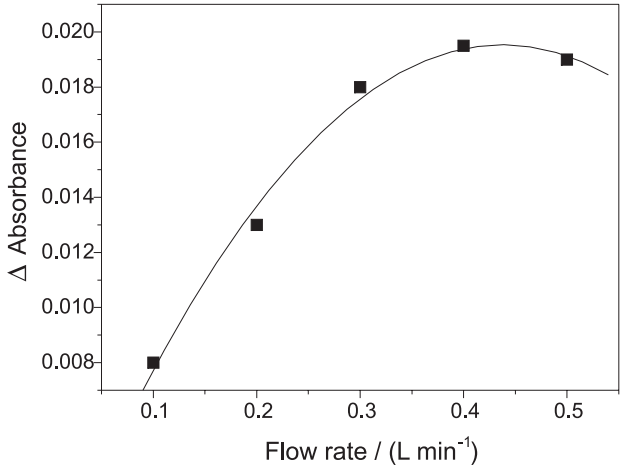

Figure 5. Analytical signal as a function of sampling flow rate. Sampling time = 5 min and $[O_3]$ = 100 ppbv.

Initially, the analytical signal increases almost linearly with increasing sampling rate and then tends to plateau, as expected for a diffusion-based sampler. The data points can be fitted by the second degree polynomial equation 4:

$$\Delta A = -3.0 \times 10^{-4} + 9.1 \times 10^{-2} V - 10.4 \times 10^{-2} V^2 \quad r = 0.9922 \quad (4)$$

where ΔA represents the difference between the analytical signals before and after ozone sampling and V is the sampling flow rate (L min^{-1}). The analytical signal linearity bias depends on the term ($-aV^2$). In physical terms linearity means that the droplet is collecting the gas with the same efficiency, independent of the amount of available ozone. It is possible to evaluate the effect of term ($-aV^2$) on the analytical signal linearity. Percentage deviations calculated from equation (4) are 12% at 0.1 L min^{-1}, 23% at 0.2 L min^{-1}, 35% at 0.3 L min^{-1}, 46% at 0.4 L min^{-1} and 58% at 0.5 L min^{-1}. For the next experiments, 0.2 L min^{-1} was the flow rate chosen, as it is a condition where the analytical signal is 77% larger than the value obtained at 0.1 L min^{-1} and the percentage deviation is only 11% higher than that obtained at 0.1 L min^{-1}.

Response characteristics

The response of the device to six different ozone concentrations, from 37 to 123 ppbv, was evaluated. The sampling flow rate was 0.2 L min^{-1} and the sampling time was 5 min. Absorbance was measured after the ozone collection and the analytical signal was linearly proportional to its concentration (equation 5).

$$\Delta A = (4.83 \pm 2.19) \times 10^{-4} + (1.23 \pm 0.03) \times 10^{-4} [O_3] \quad r = 0.9987 \quad (5)$$

where ΔA represents the difference between the analytical signals before and after ozone sampling and $[O_3]$ the ozone concentration in ppbv.

The detection limit, based on the criterion of three times the standard deviation of the blank, is better than 7.3 ppbv. However, previous experiments suggest that the detection limit can be readily improved by using a longer sampling time than 5 minutes. This result shows that the proposed method can be used in both polluted and unpolluted environments.

Possible interferences

Potential substances that might interfere with the ozone analysis were evaluated: sulfur dioxide, formaldehyde, and nitrogen dioxide. For these studies, contaminated ozone in air standard containing these compounds was prepared. Permeation sources (VICI Metronics, emitting SO_2 at 82.9 ng min^{-1}, HCHO at 69.4 ng min^{-1}, NO_2 at 93.2 ng min^{-1}) were used to generate these gases. Sulfur dioxide in a 4:1 excess over ozone and also formaldehyde in a 7:1 excess over ozone do not interfere. Nitrogen dioxide in a 6:1 excess over ozone results in a 20% positive interference. When nitrogen dioxide is in a 4:1 excess over ozone the interference is negligible. Hydrogen peroxide decolorizes the indigo solution very slowly. The selectivity of indigo is a consequence of an ozonolysis reaction. Ozone adds across the C=C double bond. The resulting bond cleavage forms colorless sulfonated isatin and similar products. At low pH, the amino groups are protonated and are therefore unreactive.[25]

Application to air samples

The present method was used to determine ozone in outdoor air in August 2004, outside of the building of the Institute of Chemistry in Araraquara, SP, Brazil. Measurements were taken every five minutes to follow the variation of ozone over the period of the day. Daytime outdoor concentrations were as high as 45 ppbv, with an increase in ozone concentration during the period of increased sunlight and decrease thereafter, similar to values for air measured in this location by direct ozone UV monitor (Thermo Environmental Instruments Inc. O_3 Analyzer 49 C).

Conclusions

We demonstrated here a new method to determine atmospheric ozone. The sensor achieved a low detection limit (7.3 ppbv) and had the advantages of being simple to construct and of having a fast response. Besides, it consumes very low amounts of reagent, and it is insensitive to common interferences such as oxidized trace species present in air. The concentrated indigo reagent is stable and can be stored for months. This monitoring device is a novel and flexible option in sampling schemes for applications related to measuring ambient ozone.

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