High Time-Resolution Optical Sensor for Monitoring Atmospheric Nitrogen Dioxide

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S *Supporting Information*

ABSTRACT: High time-resolution monitoring of nitrogen dioxide (NO_2) is of great importance for studying the formation mechanism of aerosols and improving air quality. Based on the Griess−Saltzman (GS) reaction, a portable NO_2 optical sensor was developed by employing a porous polypropylene membrane tube (PPMT) integrated gas permeation collector and detector. The PPMT was filled with GS reagents and covered with a coaxial jacket tube for gas collection. Its two ends were respectively fixed with a yellowish-green light-emitting diode and a photodiode for optic signal reception. NO_2 was automatically introduced through the collector by two air pumps cooperating with a homemade gas injector. Under the optimized conditions, the device presented good performance for monitoring NO_2, such as a limit of detection of 5.1 ppbv (parts per billion by volume), an intraday precision of 4.1% (RSD, relative standard deviation, $n = 11$, $c = 100$ ppbv), an interday precision of 5.7% (RSD, $n = 2−3$ per day for 5 days, $c = 100$ ppbv), an analysis time of 4.0 min, and a linearity range extended to 700 ppbv. The developed device was successfully applied to analyzing outdoor air with a comparable precision to that of the standard method of China. The high time-resolution characteristic that includes sampling 15 times per hour and a good stability for 10 days of urban air analysis had also been evaluated.
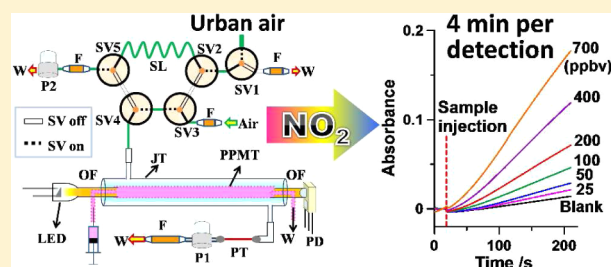
Nitrogen dioxide (NO_2) is well-known as a "criteria air pollutant" because of its role in aerosol formation, such as being a precursor of ozone and a major reactant of photochemical smog and particulate matter.[1,2] With the improvement of the quality of life and transit mobility, a growing amount of NO_2 from fossil fuel combustion has unintentionally been produced and emitted into the atmosphere.[3−5] Its arbitrary emissions have caused serious air pollution and induced various respiratory illnesses.[6−9] In order to reduce its environmental effects (e.g., acid rain, air haze, and nutrient pollution) and to prevent acute and chronic harm to public health, 1 h daily maximum concentrations of atmospheric NO_2 have been strictly regulated in China,[10] the European Union,[11] the United States,[2] and other countries.[12]

For monitoring NO_2 levels, many analytical techniques have been developed, including chemiluminescent assays,[13,14] fluorescent methods,[15−17] semiconductor gas sensors,[18,19] electrochemical sensors,[19−22] chromatographic methods,[23−25] and integrated absorption spectroscopy devices.[26,27] To date, a series of fluorescent probes and chromogenic reagents have been studied for gas sensing,[28−32] but only the Griess−Saltzman (GS) method has been proposed as the standard method for NO_2 detection in China (HJ 479−2009).[33] Although the accuracy of GS method has been validated for

dozens of years, it still suffers from its complicated procedure, time-consuming coloration, unintegrated devices, and its requirement of a large sample volume of air.

Recently, portable optical devices assembled with light-emitting diodes and photodiodes present comparable sensitivity, selectivity, and stability as commercial spectrometers for component analysis.[34−37] Based on the reactions between NO_2 and 8-amino-1-naphthol-5-sulfonic acid[34] as well as calix[4]-arenes,[38] the Dasgupta group invented two optical transmission sensors for monitoring NO_2. Besides high time-resolution performance (one sample per 5 min), their limits of detection (LOD) were 0.64 ppbv and 0.54 ppmv, respectively. In addition, the porous membrane tube has also been introduced into portable optical devices for gas collection.[39] For these devices, either the impregnated plates with chromogenic agents are needed to be freshly prepared before measurements, or the amounts and flowing rate of the gas sample are hard to control.

In this paper, we develop a portable NO_2 optical sensor by employing a porous polypropylene membrane tube (PPMT) integrated gas permeation collection and detection. An air

sample injector is employed for controlling gas amounts and flowing rate. The operating conditions for monitoring atmospheric NO_2 have been systemically studied. And the performance of the developed device has been evaluated by comparison with the standard method of China.

■ EXPERIMENTAL SECTION

Device Construction. The sketch of the developed device is shown in Figures 1 and S1. The system shown in Figure S1 is
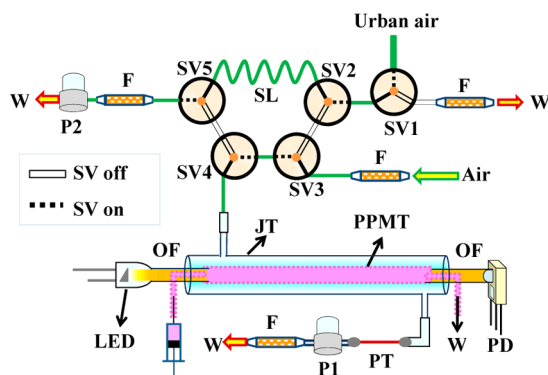

Figure 1. Schematic representation of the NO_2 detection device for urban air analysis. SV: solenoid valve; F: sodium hydroxide filter; SL: sample loop; OF: optical fiber; LED: light-emitting diode; JT: jacket tube; PPMT: porous polypropylene membrane tube; PD: photodiode; PT: peek tube; P1 and P2: air pump; W: waste.

only used for standard NO_2 detection. The standard NO_2 was prepared by two mass flow controllers (MFC, 10 SLPM and 100SCCM, Shenzhen Flow Method Measure and Control System Co., Ltd., China, www.flowmethod.net), with N_2 as dilution gas. All of the MFCs were calculated by a soap film gas flowmeter (SCal Plus, Beijing Municipal Institute of Labor Protection). In the case of standard gases prepared offline (e.g., prepared in bags), the sketch of the used device is shown in Figure 1. The gas sample injection system was assembled by five solenoid valves (SV) and a piece of PTFE tube (200 mL, i.d. = 1.0 cm, L = 128 cm). Homemade filters padded with sodium hydroxide were connected to one end of SV1, SV5, and air pump (P1) for receiving waste. Another filter connected with one entrance of SV3 was used to clean the acid and water vapor before the gas entered into the system.

The NO_2 detection cell was basically assembled by a porous polypropylene membrane tube (PPMT, Accurel PP, 1.8 mm i.d., 2.0 mm o.d., 50 mm in length) with an outer jacket tube (5.0 mm i.d., 7 mm o.d., 50 mm in length), plastic optical fibers (poly(methyl methacrylate), PMMA, 2.0 mm i.d.), a light-emitting diode (LED, 560 nm), and a light to voltage converter (Photodiode, TSL257, www.ams.com). The ends of the PPMT were connected to the polished LED and the photodiode via plastic optical fibers. Both fibers close to PPMT are machined with an L-shaped aperture (0.50 mm i.d.). The GS reagents are injected into and discharged out of the PPMT via the L-shaped apertures with two pieces of PTFE capillary tubing (PTFE extruded tubing, 0.30 mm i.d., 0.9 mm o.d., www.zeusinc.com). A coaxial outer jacket tube was used for gas diffusion collection. The two ends of the jacket tube were connected with PTFE tubing (2 mm o.d., 1.6 mm i.d.) as gas passageways. All joints were fixed with clear hot glue, and the whole detection cell was wrapped with black friction tape to eliminate interference from ambient light.

A micro air pump (P1, 310-B, 6 V, www.fspump.cn) equipped with a length of PEEK tube (PT, 0.125 mm i.d.) was used to control the gas flow rate. A plastic syringe was used to inject and change the GS reagent in the PPMT. A 16-bit USB-based data acquisition (DAQ) board (USB-1608FS-Plus) and a laptop computer were employed for converting and recording the signal change of the photodiode. A DC regulated power supply (RPS3005D-2, www.chinarek.com) and lithium-ion polymer battery (Yinuo, 12v, 80Ah) was used as the power supply in lab and in field analysis, respectively. The details of the electric circuit of LED, the light to voltage converter, DAQ, and the solenoid valves are shown in Figure S2.[40]

Reagents, Sample Information, Experimental Procedure, and Data Analysis. The details of the reagents, sample information, experimental procedure, and data analysis are shown in the Supporting Information (Reagents and samples, Experimental procedures for standard NO_2 detection, Experimental procedures for urban air analysis, and Data analysis).

■ RESULTS AND DISCUSSION

Spectrum Properties of the Light Sources and GS Reagent Solution. The Griess−Saltzman (GS) method has been approved and authorized for spectrometric determination of NO_2 in air for decades. The reaction between NO_2 and the GS reagent quantitatively produced a red-pink color azo dye that can be used for colorimetric determination of NO_2. The schematic illustration for the GS reaction is shown in Figure S3. The absorption spectrum of the GS reagent solution, the absorption spectrum of GS reagent solution with absorbed NO_2, and the LED emission spectrum are shown in Figure 2.
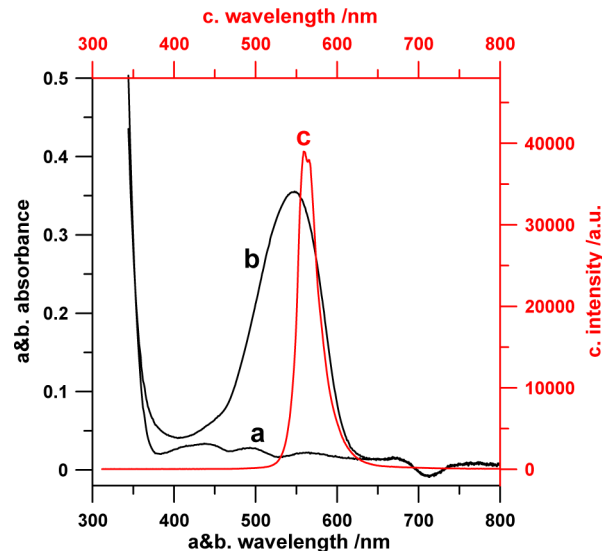

Figure 2. Spectroscopic details relevant to the measurement system. (a) Absorption spectrum of GS solution; (b) absorption spectrum of GS solution with absorbed NO_2 (1000 ppbv, 2 L of NO_2 absorbed in 10 mL of GS solution); and (c) LED emission spectrum.

As reported, the maximum absorption wavelength of the GS reagent solution with absorbed NO_2 is about 540 nm (Figure 2b), and its spectrum domain is around 400 to 640 nm. The emission wavelength of the yellowish-green LED is located between 520 to 640 nm, which is narrower than that of the GS solution absorbed NO_2 gas. As a result, this yellowish-green LED with maximum wavelength of 560 nm can be directly

employed as the light source for the NO_2 detection without any raster or optical prisms.

Effect of the Concentration of GS Solution for Monitoring NO_2. According to the standard method (HJ 479−2009), the GS solution is composed of 4.0 g L^{-1} of sulfanilic acid, 40 mL L^{-1} of acetic acid, and 0.040 g L^{-1} of n-(1-naphthyl)-ethylenediamine dihydrochloride. For obtaining good signals, reagent concentrations ranging from an 8-fold dilution to 2 times the concentration of the standard GS solution have been investigated (Figure S4a). It is obvious that the high concentration of the chromogenic reagent is beneficial for monitoring NO_2. However, it is difficult to prepare high levels of sulfanilic acid due to its limited solubility in water. In order to avoid the PPMT being blocked by the crystallization of sulfanilic acid, the regular concentration of GS solution is used in the following study.

Effect of the Air Flow Rate for Monitoring NO_2. Generally, the traditional GS reaction for detecting NO_2 could be completed in about 15 min. In this device, the GS reaction initially occurs on the gas−liquid interface. Its reaction process is closely related to the gas diffusion rate and reaction time, which are obviously affected by the gas flow rates.

In order to acquire the steady flow rate, a piece of red peek tube (PT in Figure 1, i.d. 125 μm, o.d. 1.6 mm) is fixed between the air pump and the detection cell for controlling the gas flow rate. It has been found that the length of the tube can dramatically affect the signals (Figure S4b). Without the peek tube, the gas flow rate is about 1.0 L min^{-1}, and it only takes ca. 12 s to finish the adsorption process, i.e., 200 mL of air sample completely passing through the detection cell. However, the high flow rate leads to incomplete absorption and color reaction. With the PT length increased from 0 to 2 cm (i.e., decreasing the air sample flow rate), the normalized signals rise simultaneously. Further increases of the PT length leads to no obvious, observable change of the signals. For further studies, a piece of PEEK tubing of 2.0 cm was adopted as the junction to control the air flow rate. In this case, the air flow rate is at about 50 mL min^{-1} as measured by the soap film flow meter.

Performance of the Device for Monitoring NO_2. Under the optimized conditions, the standard NO_2 gas (25 to 1000 ppbv) has been successfully detected by the assembled device. The linearity range extends to 700 ppbv with the coefficient of determination (R^2) of 0.9925 (Figure S5). When the concentrations of NO_2 are above the stated range (>1000 ppbv), a quadratic calibration equation can be used for its calibration. Since NO_2 concentrations in urban air are generally below 1000 ppbv, high levels of NO_2 have not been investigated in this study. The limit of detection (LOD, S/N = 3) for monitoring atmospheric NO_2 is 5.1 ppbv, and the relative standard deviation (RSD) is 4.1% for 11 successive determinations of 100 ppbv of NO_2. Each run for monitoring NO_2 can be finished in 4 min, containing about 200 s for data acquisition and about 40 s for sample loading and GS reagent solution changing. This indicates that the time resolution of our device is of 15 h^{-1}. The interday precision has also been evaluated, with an RSD of 5.7% (n = 2−3 per day for 5 days, c = 100 ppbv). The interday calibration curves (n = 5 day) are summarized in Table S1 and Figure S6. There is no significant difference for the interday calibration curves in 5 days, indicating the excellent stability of the developed device for monitoring interday NO2.

The potential interferent effects have been tested by spiking a certain amount of NO, SO_2, H_2S, NH_3, and CO_2 in the

detection of NO_2 by using the device. The experimental results confirm that for 100 ppbv of NO_2 and within a ± 5% error range, 2000 ppbv of NO, SO_2, H_2S, and NH_3, and 500 000 ppbv of CO_2 do not interfere with the detection of NO_2. In addition, because the GS reagent solution is kept in the PPMT with the nominal pore size of 0.2 μm, the dominant interferent effects from atmospheric particulate matters are coincidentally avoided. The selectivity of the developed device should be better than the standard method (HJ 479−2009) and appropriate for the detection of NO_2 in urban air.

Validation and Application of the Device for Urban Air Analysis. The performance of the assembled device has been evaluated by monitoring NO_2 in urban air samples. Air samples collected in air bags from Songling Road and the QIBEBT campus have been analyzed by the assembled device and the standard method (HJ 479−2009), respectively (Table 1). For the standard method, due to the different coexisting

Table 1. Analytical Results of NO_2 Concentrations Determined in Urban Air by the Assembled Device and the Standard Method (HJ 479-2009)

date	sampling location	present method/ ppbv	standard method/ ppbv
Jan. 21	QIBEBT campus	50.0 ± 13.7	53.3 ± 25.0
Jan. 22	QIBEBT campus	111.8 ± 12.4	114.8 ± 14.1
Feb. 23	Songling road side	144.6 ± 4.7	151.3 ± 7.9
Mar. 01	Songling road side	223.5 ± 7.2	225.6 ± 7.5

species with various concentration levels in each sample, the interferent effects are varied in each detection, leading to the diverse deviations of the detection results. Through application of the similar colorimetric mechanism, the similar trend of the deviations between the present method and the standard method (HJ 479−2009) is expected. The results obtained by our device are highly consistent with those of the standard method, indicating its candidate role of the standard method. Additionally, its application potential has also been evaluated by continuously monitoring atmospheric NO_2. The results from air samples collected at the same locations in 10 different days (March 16~25, 2017) and in certain periods of one day are shown in Figure 3. NO_2 levels in the QIBEBT campus are all slightly lower than that of the Songling Road roadside (Figure 3a,b), corresponding to its distance from Songling Road (i.e., > 50 m). For the air samples in certain periods of 1 day, the variations of atmospheric NO_2 can be distinguished and recorded at every 4 min (Figure 3c). For example, the NO_2 concentrations in the QIBEBT campus were at a low level (0−50 ppbv) from 2:55 to 3:24 p.m., while it increased to 100 ppbv rapidly after 3:24 p.m. and then kept at a high level (ca. 100−200 ppbv) until about 5:26. The results were in agreement well with the vehicular traffic activities on Songling Road, where heavy traffic starts at around 3:30 p.m. The vehicle exhaust gas was further confirmed as a main source of NO_2 in urban air.

■ CONCLUSION

By employing a light-emitting diode as the light source, a photodiode as the detector, and the Griess−Saltzman reaction as the quantitation basis, a high time-resolution optical sensor for monitoring atmospheric NO_2 has been developed. The device presents a set of excellent properties, such as good intraday and interday precision, a low RSD and LOD, and high time resolution. When used for monitoring NO_2 in the urban
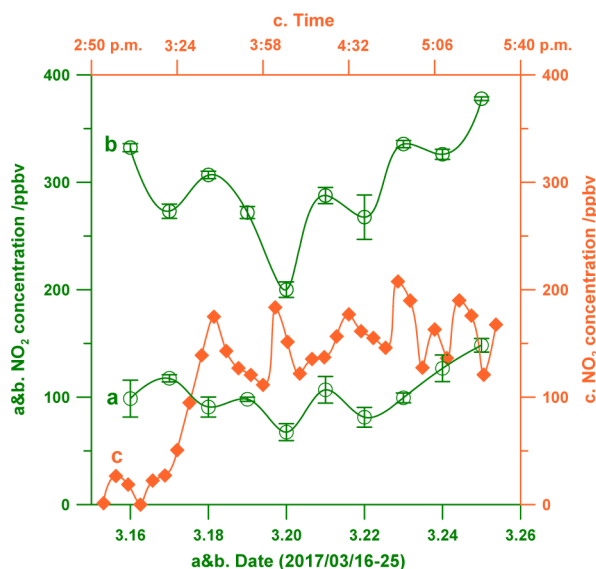
Figure 3. (a,b) Results of NO$_2$ concentration detected in the air of the QIBEBT campus (a) and Songling Road side (b) from March 16 to 25. (c) The NO$_2$ concentration monitored by the device from 2:55 to 5:30 p.m. on the QIBEBT campus (time solution 15 h^{-1}).

air, the variations in periods of 10 days (one sample per day) and about 3 h (one sample per 4 min) can be precisely recorded. The results suggested that the developed device has great potential in routine NO$_2$ analysis in both the laboratory and the field.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.7b03578.

> Reagents and samples, experimental procedures for standard NO$_2$ detection, experimental procedures for urban air analysis, data analysis, additional figures, and tables (PDF)

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Notes

The authors declare no competing financial interest.

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