

Research Article

Determination of Nitrogen Oxides with Rhodamine B by Fluorescence Quenching Method

Yan Pugen,¹ Qiu Haiou,¹ Lu Cuili,² and Tang Zhiyong¹

¹ Faculty of Material Sciences and Chemical Engineering, China University of Geosciences, Wuhan 430074, China

² Hubei Gedian Humanwell Pharmaceutical Co. LTD, Wuhan 430074, China

Correspondence should be addressed to Lu Cuili, xiaol114@yahoo.cn

Received 26 November 2010; Revised 16 January 2011; Accepted 6 February 2011

Academic Editor: Veronica Vaida

Copyright © 2011 Yan Pugen et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

NO₂ can be transformed into nitrite by the absorption of Rhodamine B solution, which will make fluorescence quenching of Rhodamine B in acidic medium. According to this mechanism, a new method for detecting nitrogen oxides in the air is developed by a fluorescence spectrophotometry. The influence of environmental media and interfering substances in the fluorescence intensity of system was studied. Under the optimal experimental conditions, the decrease of fluorescence intensity varies linearly with the concentration of NO₂⁻ over the range of 0.009~0.500 μg/ml with a correlation coefficient of 0.9992. The method is simple and has a lower limit of detection than the common methods. It can be a referee for the environmental evaluation.

1. Introduction

Nitrogen oxides are one of the main pollutants as well as the evaluation criteria of the air quality. Nitrogen oxides in the atmosphere have harmful effects on humans mainly through the respiratory system, which may cause acute and chronic poison. Therefore, the study of analysis and detection methods for nitrogen oxides will be significant. There are many methods for the determination of nitrogen oxides such as ion chromatography [1], chemiluminescence [2, 3], fluorescence [4], and colorimetric microdetermination [5]. However, the method that nitrogen oxides in the air were determined with Rhodamine B by fluorescence quenching has not been reported.

Nitrogen oxides can exist in various forms including the main forms of NO and NO₂ in the atmosphere. In this research, the contents of NO and NO₂ in the air sample were determined indirectly by measuring the content of nitrite and solution absorption-fluorescence spectrometry. There are many methods for the determination of nitrite such as spectrophotometry [6–8], fluorescence [9–14], chemiluminescence [15–17], polarography [18] and chromatography [19–22]. Among these methods, the fluorescence method has attracted much attention and been applied widely for the detection of nitrite for the high sensitivity, selectivity, low

limit of detection and simple operation. According to the literature, NO₂⁻-organic dyes and NO₂⁻-KBrO₃⁻-organic dyes are the main systems for the determination of nitrite by the fluorescence spectrometry.

The common determination of nitrogen oxides is Saltzman method [23, 24]. However, the contents of NO and NO₂ in the actual air sample are determined with Rhodamine B by fluorescence quenching with quite satisfactory results. The method in the text is simple and has a lower limit of detection, which provides a referee for the assessment of environment.

2. Experimental Section

2.1. Instruments and Reagents. An LS-55 fluorescence spectrophotometry instrument (PerkinElmer Limited) equipped with a 1 cm×1 cm quartz cell, an HHS electrothermal thermostatic water-bath pot (Shanghai Boxun Co.), air sampler (Wuhan Tianhong TH-110B type), porous glass plate absorbs bottles packed with 10 mL absorbing liquid for short time sampling.

Nitrite working solution (5.0 μg/mL) was prepared by diluting the stock solution (1.0 g/L) before use. Rhodamine B working solution (5.0×10⁻⁶ mol/L), sulfuric acid solution,

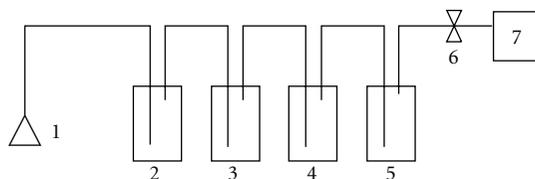


FIGURE 1: The scheme of air sampling device. (1) air inlet, (2) absorb bottle, (3) bottle of acidic potassium permanganate, (4) absorb bottle, (5) buffer bottle, (6) flowmeter, (7) Air sampler.

sodium acetate solution (2.0 mol/L). Absorbing liquid was prepared as follows. 4 mL of sulfuric acid solution (0.1 mol/L) and 12.00 mL of Rhodamine B solution was added into a 100 mL volumetric flask and diluted with the distilled water. Oxidation liquid (0.16 mol/L) was prepared by dissolving 2.5286 g of potassium permanganate in 50 mL of water with slight fever, in which 50 mL of sulfuric acid solution (1 mol/L) 50mL was added. The prepared solution was stored in brown reagent bottle. All chemicals were of analytical grade and used without further purification. All solutions were prepared with ultrapure water.

2.2. Experimental Methods

2.2.1. Air Sample Collection and Processing. Nitrogen oxides in the air were determined actually by measuring the contents of NO_2 and NO . NO_2 can be absorbed directly by the absorption solution while NO cannot be adsorbed. Therefore, to determine the amount of nitrogen oxides, NO must be oxidized firstly to NO_2 . In our research, NO was oxidized by 10.0 mL of acidic potassium permanganate solution and the volume of absorption solution was 10.0 mL. The scheme of air sampling device is shown in Figure 1.

The expression of concentration is given as follows:

$$C_{\text{NO}_x} = C_{\text{NO}_2} + C_{\text{NO}}, \quad (1)$$

$$C_{\text{NO}_2} = \frac{(\Delta F_1 - a) \cdot V}{b \cdot f \cdot V_0}, \quad (2)$$

$$C_{\text{NO}} = \frac{(\Delta F_2 - a) \cdot V}{b \cdot f \cdot k \cdot V_0}, \quad (3)$$

where C_{NO_x} : concentration of nitrogen oxides in the air, mg/m^3 ; C_{NO_2} : concentration of nitrogen dioxide in the air, mg/m^3 ; C_{NO} : concentration of nitric oxide in the air, mg/m^3 ; ΔF_1 , ΔF_2 : difference between the value of fluorescent signal of the first and the second branch absorption in bottle sample and the value of blank signal, respectively; b , a : slope ($\Delta F \cdot \text{mL}/\mu\text{g}$) and intercept of linear regression equation of standard curve, respectively; V : volume of the absorption solution, mL; V_0 : volume of the sample under standard state (101.325 kPa, 273 K), L; K : oxidation coefficient of $\text{NO} \rightarrow \text{NO}_2$, 0.68; and F : coefficient of Saltzman experiment, 0.88 (it is 0.77 when the content of NO_2 in the air is higher than 0.720 mg/m^3).

2.2.2. Determination Method. 1.00 mL of H_2SO_4 solution (0.1 mol/L), 3.00 mL of Rhodamine B solution ($5.0 \times$

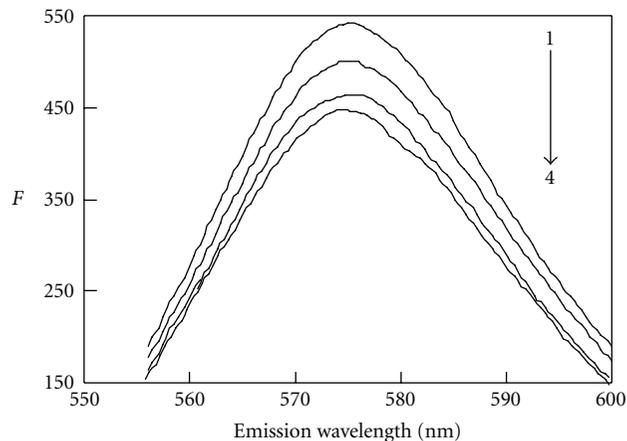


FIGURE 2: Fluorescence emission spectra. (1) Rhodamine B + H_2SO_4 + NaAc, (2) Rhodamine B + H_2SO_4 , (3) Rhodamine B + H_2SO_4 + NO_2^- + NaAc, (4) Rhodamine B + H_2SO_4 + NO_2^- . Rhodamine B: 6.0×10^{-7} mol/L, H_2SO_4 : 4.0×10^{-3} mol/L, NO_2^- : 0.4 $\mu\text{g}/\text{mL}$, NaAc: 0.08 mol/L, temperature: 60°C, time: 45 minutes.

10^{-6} mol/L), and a certain amount of nitrite standard solution were added in sequence into a 25 mL colorimetric tube, which was diluted with water to total volume of 25 mL and shaken before it was placed in a water bath (60°C) for 45 minutes. Then, the colorimetric tube was taken out for cooling. 1.00 mL of sodium acetate solution (2.0 mol/L) was added further into the above solution and shaken well. The excitation and emission wavelengths were 555 nm and 576 nm, respectively. The fluorescence intensity of both sample solution (F) and corresponding blank solution (F_0) was detected. The value of $\Delta F(F_0 - F)$ was recorded.

3. Results and Discussion

3.1. Excitation and Emission Spectrum. Rhodamine B is a kind of pinkish synthetic dye, which has intense fluorescence in solution and has been used commonly in fluorescent dye of cell, colored glass, and characteristic fireworks, and so forth. Figure 2 shows the fluorescence emission spectra of different Rhodamine B systems. It can be found that the fluorescent intensity of Rhodamine B decreases with the addition of NO_2^- (curve 4) in the system of Rhodamine B + H_2SO_4 (curve 2). Curve 1 and 3 shows that the system can be activated when an appropriate amount of sodium acetate is added. In addition, there is a linear relationship between the concentration of NO_2^- and ΔF under certain conditions. It can be concluded that a method for the determination of NO_2 and NO is developed by fluorescence spectrophotometry. The maximum excitation and emission wavelengths for the system are 555 nm and 576 nm, respectively.

3.2. Influence of Reaction Media. The influence of reaction media in ΔF was analyzed. Different acidic media was investigated, such as sulfuric acid, hydrochloric acid, acetic acid, phosphoric acid, and nitric acid. The highest sensitivity was detected in the sulfuric acid media. Therefore, sulfuric

TABLE 1: Results of the determination of NO_x in the air samples.

Place of sample	Average concentration of NO _x per hour (mg/m ³)	RSD (%) (n = 6)	Saltzman method	Method recovery (%)
Laboratory	0.0297	3.4	0.0304	104.7
Outside of laboratory	0.0095	7.4	0.0086	97.8
A gymnastical zone	0.0029	8.2	—	91.5

acid was used in this experiment. In addition, the effect of dosage of sulfuric acid (0.1 mol/L) was also studied in the range of 0.2~2.00 mL. It was found that the maximum value of ΔF could be obtained as the dosage was 1.00 mL. Then, 1.00 mL of sulfuric acid solution was used in the experiment.

3.3. Influence of Dosage of Rhodamine B. The influence of Rhodamine B solution (5.0×10^{-6} mol/L) in ΔF was also studied. Results indicated that fluorescent signal of the system increased gradually with the increased Rhodamine B dosage while the value of ΔF increased firstly and then decreased. The maximum value of ΔF was obtained when the dosage of Rhodamine B was 3.00 mL. Therefore, 3.00 mL of Rhodamine B was chosen as optimum dosage in the further studies.

3.4. Influence of Dosage of Activator. Different materials were used to study the influence of activator, such as sodium citric acid, citric acid, sodium acetate, oxalic acid, sodium phosphoric acid and sodium dodecyl sulfonic acid. Both the improved fluorescence intensity and value of ΔF were detected by using the sodium acetate. Furthermore, the largest value of ΔF could be obtained for the 1.00 mL of sodium citrate solution (2.0 mol/L). Hence, 1.00 mL of sodium citrate was chosen in the experiment.

3.5. Influence of Reaction Temperature. The influence of temperature on the value of ΔF was tested in the range of 25~80°C. It was found that the value of ΔF increased gradually with the increased temperature. Moreover, the value of ΔF was relatively constant in the range of 60°C-80°C. Then, the reaction temperature was performed at 60°C in the experiment.

3.6. Influence of Reaction Time. The variation of the value of ΔF was studied with the operation time. It was found that the value of ΔF increased fast with the prolonged reaction time in 40 minutes. The stable values of ΔF was observed with the further increased reaction time. The reaction time was chosen at 45 minutes in this experiment.

3.7. Stability Test. The fluorescence intensity was recorded after the reaction was terminated for 4 hours. The decreased fluorescence intensity was observed in 2 hours. However, the value of ΔF was unchanged, which indicated that this system was comparatively stable. Therefore, the determination could still be carried out in 2 hours.

3.8. Working Curve and Limit of Detection. Under the optimal conditions described above, a linear relationship between the concentration of NO₂⁻ and the value of ΔF was obtained in the concentration range of 0.009 ~0.500 $\mu\text{g/mL}$ of NO₂⁻. The linear regression equation is

$$\Delta F = 49.042\rho (\mu\text{g/mL}) - 1.098. \quad (4)$$

The correlation coefficient (r) was 0.9992. The limit of detection was calculated to be 0.003 $\mu\text{g/mL}$ by $3\text{Sb}/k$ (Sb the standard deviation of blank, and k the slope of linear calibration). The relative standard deviation ($n = 10$) was 3.23% for 0.25 $\mu\text{g/mL}$ NO₂⁻. The limit of detection of NO₂ was 0.004 mg/m³ as 30 L solution was sampled by 10 mL of absorbing solution.

3.9. Influence of Coexistent Ion. In order to examine the effect of foreign ions in the air on the determination of nitrite, a number of ions were investigated according to the recommended procedure. The maximum error was restricted to be $\pm 5\%$ for the 0.25 $\mu\text{g/mL}$ nitrite. The limits of the tolerant foreign ions (by times) were Cl⁻ (10,000), CO₃²⁻ and SO₄²⁻ (3000), PO₄³⁻ (900), Br⁻ (700), NH₄⁺ and F⁻ (600), Formaldehyde and NO₃³⁻ (500), I⁻ and SO₃³⁻ (110), and Pb²⁺ (21), respectively. It could be seen that most of ions, even in a large excess, did not interfere with the detection.

4. Determination of Samples

Gas samples were sampled with a speed of 0.2 L/min for 2.5 hours. The content of targets can be calculated according to the fluorescent intensity of the absorbing liquid in two absorb bottles. The method has been applied to determine the concentration of NO_x in the atmosphere of a laboratory building and make the comparison with Saltzman method. The breakthrough point is that the limit of determination is lower than Saltzman method. The results are shown in Table 1.

5. Conclusion

In summary, this paper has established a new method of the concentration of NO₂ and NO in the air detected by the fluorescence quenching method, determination results were lower than air quality standards stipulated in the standard (0.24 mg/m³). The method is simple and has a low limit of detection. It can be a referee for the environmental evaluation.

Acknowledgments

The authors are thankful for the help from Song Hu-Yao for the discussion, and the members in our lab are acknowledged.

References

- [1] Y. Komazaki, H. Shimizu, and S. Tanaka, "A new measurement method for nitrogen oxides in the air using an annular diffusion scrubber coated with titanium dioxide," *Atmospheric Environment*, vol. 33, no. 27, pp. 4363–4371, 1999.
- [2] M. J. Navas, A. M. Jiménez, and G. Galán, "Air analysis: determination of nitrogen compounds by chemiluminescence," *Atmospheric Environment*, vol. 31, no. 21, pp. 3603–3608, 1997.
- [3] Y. Wang, S. H. Fan, and S. L. Wang, "Chemiluminescence determination of nitrogen oxide in air with a sequential injection method," *Analytica Chimica Acta*, vol. 541, no. 1-2, pp. 131–136, 2005.
- [4] X. Q. Zhan, D. H. Li, H. Zheng, J. G. Xu, and Y. Q. Zhou, "Fluorimetric determination of nitrogen oxides in the air by a novel red-region fluorescent reagent," *Talanta*, vol. 58, no. 5, pp. 855–860, 2002.
- [5] B. E. Saltzman, "Colorimetric microdetermination of nitrogen dioxide in the atmosphere," *Analytical Chemistry*, vol. 26, no. 12, pp. 1949–1955, 1954.
- [6] H. Weiping and D. Xuezhi, "Determination of trace nitrite by catalytic spectrophotometric method with methyl violet," *Analytical Laboratory*, vol. 16, no. 1, pp. 59–62, 2005.
- [7] K. Jichuan, M. Juan, Y. Hong et al., "Spectrophotometry determination of trace nitrite in food products," *Chinese Journal of Spectroscopy Laboratory*, vol. 26, no. 3, pp. 541–543, 2009.
- [8] C. Xing-Chen, "Determination of trace nitrite by catalytic spectrophotometry with basic fuchsin," *Chinese Journal of Spectroscopy Laboratory*, vol. 26, no. 3, pp. 724–726, 2009.
- [9] F. Suling, T. Anna, and F. Jing, "Determination of nitrite by fluorimetric method," *Analytical Laboratory*, vol. 2, pp. 41–43, 2001.
- [10] R. Huiujan and Y. Liping, "Fluorophotometric determination of nitrite with tyrosine," *Analytical Laboratory*, vol. 22, no. 1, pp. 90–91, 2003.
- [11] K. Jichuan, N. Jianping, Z. Na et al., "A fluorescence quenching method for determination of trace nitrite," *Analytical Laboratory*, vol. 24, no. 7, pp. 7–9, 2005.
- [12] N. Jie, J. Yang, and F. Meng, "Fluorimetric determination of nitrite," *Talanta*, vol. 40, no. 7, pp. 1009–1011, 1993.
- [13] L. Jingguo, W. Yaorong, and T. Yalian, "Determination of trace nitrite based on fluorescence quenching with I—Rhodamine B system," *Chinese Journal of Analytical Chemistry*, vol. 25, no. 5, pp. 590–593, 1997.
- [14] X. Zhang, H. Wang, N. N. Fu, and H. S. Zhang, "A fluorescence quenching method for the determination of nitrite with Rhodamine 110," *Spectrochimica Acta A*, vol. 59, no. 8, pp. 1667–1672, 2003.
- [15] W. Wane, D. Yong, W. Tiansheng et al., "Determination of NO_2^- in air by chemiluminescence detection," *Environmental Science and Technology*, vol. 32, no. 10, pp. 133–136, 2009.
- [16] W. Wane, W. Tiansheng, and Z. Zeyang, "Determination of trace nitrite in water using potassium bromate-acid chrome blue K chemiluminescent method," *Journal of Analytical Science*, vol. 24, no. 3, pp. 327–330, 2008.
- [17] M. Glasius, M. F. Carlsen, T. S. Hansen, and C. Lohse, "Measurements of nitrogen dioxide on Funen using diffusion tubes," *Atmospheric Environment*, vol. 33, no. 8, pp. 1177–1185, 1999.
- [18] Z. Gao, G. Wang, and Z. Zhao, "Determination of trace amounts of nitrite by single-sweep polarography," *Analytica Chimica Acta*, vol. 230, no. 1, pp. 105–112, 1990.
- [19] W. S. Jobgen, S. C. Jobgen, H. Li, C. J. Meininger, and G. Wu, "Analysis of nitrite and nitrate in biological samples using high-performance liquid chromatography," *Journal of Chromatography B*, vol. 851, no. 1-2, pp. 71–82, 2007.
- [20] N. Lohumi, S. Gosain, A. Jain, V. K. Gupta, and K. K. Verma, "Determination of nitrate in environmental water samples by conversion into nitrophenols and solid phase extraction-spectrophotometry, liquid chromatography or gas chromatography-mass spectrometry," *Analytica Chimica Acta*, vol. 505, no. 2, pp. 231–237, 2004.
- [21] I. Sarudi and I. Nagy, "A gas chromatographic method for the determination of nitrite ions in natural waters," *Talanta*, vol. 42, no. 8, pp. 1099–1102, 1995.
- [22] Y. Miura and H. Hamada, "Ion chromatography of nitrite at the ppb level with photometric measurement of iodine formed by post-column reaction of nitrite with iodide," *Journal of Chromatography A*, vol. 850, no. 1-2, pp. 153–160, 1999.
- [23] B. E. Saltzman, "Colorimetric microdetermination of nitrogen dioxide in the atmosphere," *Analytical Chemistry*, vol. 26, no. 12, pp. 1949–1955, 1954.
- [24] Y. Y. Zhou, S. K. She, Q. Lu, C. Q. Zhu, and L. Wang, "Highly sensitive spectrofluorimetric determination of trace amounts of nitrite with N-(1-naphthyl) ethylenediamine," *Spectroscopy and Spectral Analysis*, vol. 25, no. 8, pp. 1318–1321, 2005.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

