

## SHORT COMMUNICATION

### A SENSITIVE SPECTROPHOTOMETRIC DETERMINATION OF NITROGEN DIOXIDE IN THE WORKING ATMOSPHERE

Prachi Parmar<sup>1\*</sup>, Ajai K. Pillai<sup>1</sup> and Vinay K. Gupta<sup>2</sup>

<sup>1</sup>Department of Chemistry, Govt. V.Y.T. Autonomous College Durg, Chhattisgarh, India, 491001

<sup>2</sup>School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, Chhattisgarh, India, 492001

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**ABSTRACT.** In the present investigation, a simple and sensitive spectrophotometric method for the determination of nitrogen dioxide in various environmental samples is described. Nitrogen dioxide in air was fixed as nitrite ion in alkaline sodium arsenite absorbing solution. The nitrite formed was diazotized with *p*-aminoacetophenone in acidic medium which was subsequently coupled with phloroglucinol to give yellow-orange dye in alkaline medium having an absorption maximum at 420 nm. Beer's law was obeyed in the range of 0.008 - 0.12  $\mu\text{g mL}^{-1}$  of nitrogen dioxide and has a molar absorptivity of  $2.875 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ . Optimum reaction conditions for diazotization, full colour development and the effect of variables like temperature, time and pH have been studied. Detailed studies to check the collection efficiency and  $\text{NO}_2:\text{NO}_2^-$  stoichiometric ratio has been carried out. The reaction has been successfully applied for the detection of nitrogen dioxide in cigarette smoke, scooter exhaust, and workroom air.

**KEY WORDS:** Non-extractive spectrophotometry, *p*-Aminoacetophenone, Phloroglucinol, Nitrogen dioxide

## INTRODUCTION

Nitrogen dioxide is one of the most hazardous pollutants among the oxides of nitrogen and plays an important role in the formation of acid rain [1], photochemical smog, photochemical oxidant such as ozone and peroxyacetyl nitrate (PAN) and in generation of many secondary pollutants [2]. The major sources of  $\text{NO}_x$  pollution are fossil fuel combustion in power stations,  $\text{N}_2$  in air and nitrogen in the fuel which are oxidized to NO. Nearly half of all anthropogenic  $\text{NO}_x$  emissions come from mobile sources, the remainder coming from power stations and industrial boilers. Natural sources of  $\text{NO}_x$  include volcanoes, bacterial activity, forest fires and lightning. Traffic is estimated to contribute as much as half of the total nitrogen dioxide emission [3]. Cigarette smoke and auto-exhaust are also reported to contain significant amount of nitrogen dioxide [4]. Exposure to nitrogen dioxide can irritate the lungs and lower the resistance to respiratory infections (e.g. influenza), particularly in people with existing respiratory illness, such as asthma. The effect of short-term exposure to nitrogen dioxide are still unclear, but continued or frequent exposure to concentration higher than those normally found in the ambient air may cause increased incidence of acute respiratory illness in children [5]. Indoor nitrogen dioxide which is produced by gas or other fuels used for heating and cooking, was found to exhibit increased respiratory symptoms, decreased pulmonary lung function, respiratory illness, increased incidences of chronic cough, conjunctivitis, bronchitis, and asthma exacerbation [6, 7].

Various methods are available for the determination of nitrogen dioxide such as fluorimetric [8], flow injection method [9], laser induced fluorescence [10], field modulation laser spectroscopy [11], tunable diode laser, droplet method [12], amperometric [13], gas

\*Corresponding author. E-mail: pracheeparmar@gmail.com

chromatography [14], liquid chromatography [15], chromatomembrane cell [16], fiber optic spectroscopy [17], piezo-dosimeter [18], and passive sampling devices [19], etc. A large number of spectrophotometric methods are also reported in the literature for the detection and determination of nitrogen dioxide [20-21].

The proposed method is rapid and free from rigorous control of experimental condition. Simple equipment, stability of colour, non-toxic nature of reagents and its easy availability are added advantages. In this paper, a reagent system based on the Greiss reaction is described. Nitrogen dioxide in air is fixed as nitrite ion then nitrite ion diazotized with *p*-aminoacetophenone and the diazonium ion obtained is coupled with phloroglucinol in alkaline medium to give a yellow-orange dye. The method has been applied for routine analysis of nitrogen dioxide in air.

### EXPERIMENTAL

*Apparatus.* A Toshniwal model TVSP 25 spectrophotometer (India) with 1.0 cm matched quartz cell was used for all absorbance measurement. Fritted glass bubblers with suitable suction devices were used for trapping nitrogen dioxide from air. The flow rate of air was measured using a rotameter. pH measurements were made with Systronics pH meter model 331 (India).

*Reagents.* All the chemicals used were of analytical reagent grade or the best quality available. Double distilled deionised water was used throughout the experiment. A stock solution of nitrite containing  $1000 \mu\text{g mL}^{-1}$  of nitrite was prepared by dissolving 0.15 g of pre-dried sodium nitrite (Loba Chemie, Mumbai, India) in 100 mL of nitrite free water. Few drops of chloroform were added as stabilizer. Working solution of nitrite was prepared by appropriate dilution of stock solution. 0.2% *p*-aminoacetophenone (Loba Chemie, Mumbai, India) was prepared in 1:4 hydrochloric acid. 0.1% phloroglucinol (Merck, Mumbai, India) was prepared in aqueous solution. Alkaline sodium arsenite absorbing solution was prepared by dissolving 0.1 g of sodium arsenite in 100 mL of 0.1 M sodium hydroxide. The solution stored at 4 °C was stable for ~ 2 weeks. 1 M sodium hydroxide solutions was prepared to obtain required alkalinity. A 10% w/v aqueous solution of disodium salt of EDTA (Merck, Mumbai, India) was prepared for masking ions.

*Procedure.* An aliquot of a solution containing 0.2 to 2  $\mu\text{g}$  of nitrite was taken in an impinger. Nitrogen dioxide was liberated from the aliquot by adding 6.0 M hydrochloric acid drop-wise from a micro-burette. The liberated nitrogen dioxide was absorbed in the absorbing solution taken in two midjet impingers of 35 mL capacity each containing 10 mL of absorbing solution connected to a source of suction. After sampling, the absorbing solution was transferred into a 25 mL measuring flask and then 1 mL PAAP was added. The solution was kept for 2 min in ice bath then 1 mL of phloroglucinol was added. The solution was made alkaline with sodium hydroxide resulting in the formation of yellow-orange dye. The absorbance of the dye was measured at 420 nm. Amount of nitrogen dioxide was deduced from the calibration graph prepared for 0.2 to 2  $\mu\text{g}$  of nitrite after correction with stoichiometric factor, i.e. 0.75.

*Determination of nitrogen dioxide in cigarette smoke.* Absorbing system consisting of glass wool (to remove the particulate matter), followed by three midjet impingers, the first two containing acidic potassium permanganate (2.5%  $\text{KMnO}_4$  (w/v) in 2.5%  $\text{H}_2\text{SO}_4$ ) for oxidation of nitric oxide to nitrogen dioxide and third impinger containing 10 mL of absorbing solution for collection of cigarette smoke was set up (Figure 1). A cigarettes marked to a required length was fixed in a glass holder placed in the tip of suction hole of the first impinger. It was lighted and the air was sucked at a rate of  $0.75 \text{ L min}^{-1}$  till it burned to the marked length. The collected gas was analyzed for nitrogen dioxide as recommended in the procedure.

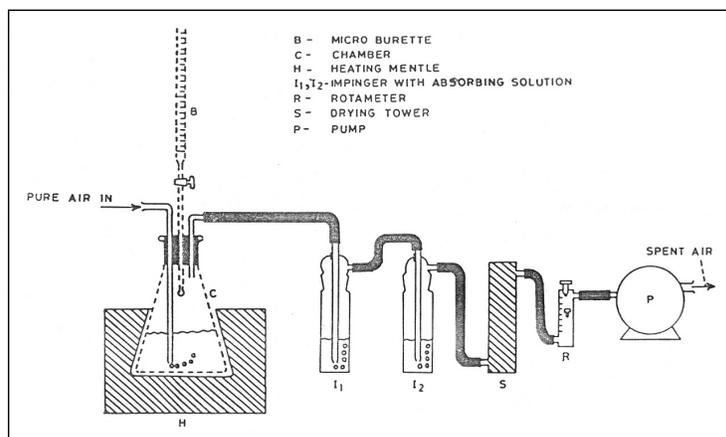
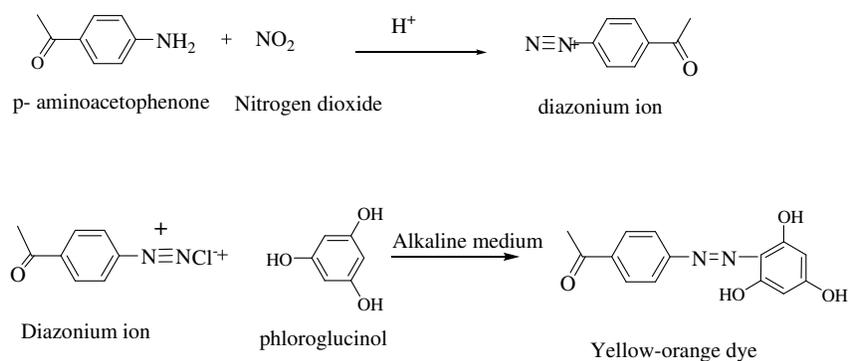


Figure 1. Assembly train for sampling of air pollutants.

*Auto exhaust applications.* Auto exhaust gases from automobile were drawn through two midget impingers each containing 5 mL of absorbing solution attached to a suction pump. The gas was analysed for nitrogen dioxide by the proposed method.

*Determination of nitrogen dioxide in work-room air.* Air samples were drawn through two 35 mL calibrated midget impinger containing 5 mL of absorbing solution connected in series at a flow rate of  $0.75 \text{ L min}^{-1}$ . Amount of nitrogen dioxide was determined by the proposed method.

*Colour reaction scheme.* The colour reaction involves two steps: (1) *p*-aminoacetophenone reacts with nitrogen dioxide to form acetophenone diazonium chloride and (2) diazonium ion is coupled with phloroglucinol to give yellow-orange coloured dye having  $\lambda_{\text{max}}$  420 nm.



## RESULTS AND DISCUSSION

*Analytical data.* A linear calibration graph was obtained for  $0.008\text{--}0.12 \mu\text{g mL}^{-1}$ . The detection limit of nitrogen dioxide was  $0.007 \mu\text{g mL}^{-1}$ . Precision of method was established by determining the concentration of 6 samples containing  $2 \mu\text{g}$  of nitrogen dioxide; the relative standard deviation was 0.26%. The calibration graph has a correlation coefficient of 0.9753.

The molar absorptivity of the colour system was  $2.875 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  at 420 nm (Figure 2) and the Sandell's sensitivity was  $0.00016 \text{ mg cm}^{-2}$ . The slope, the intercept, and the correlation coefficient evaluated by a least-squares regression analysis were also included (Table 1).

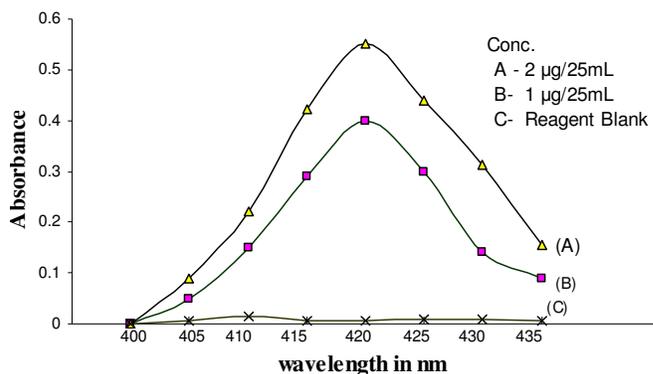


Figure 2. Absorption spectra of the dye.

Table 1. Spectral characteristics, precision and accuracy of the presented method.

Parameter	Results
Stability of colour (hours)	~ 72
$\lambda_{\text{max}}$ (nm)	420
Limit of Beer's law ( $\mu\text{g mL}^{-1}$ )	0.008-0.12
Molar absorptivity ( $\text{L mol}^{-1}\text{cm}^{-1}$ )	$2.875 \times 10^5$
Limit of detection ( $\mu\text{g mL}^{-1}$ )	0.007
Limit of quantification ( $\mu\text{g mL}^{-1}$ )	0.022
Sandell's sensitivity ( $\mu\text{g cm}^{-2}$ )	0.00016
Standard deviation ( $\pm$ )	0.0015
Relative standard deviation (%)	0.26
Regression equation ( $Y = bx + a$ ) <sup>*</sup>	
Slope b	2.9111
Intercept a	0.2379
Correlation coefficient ( $r$ ) <sup>**</sup>	0.9753

<sup>\*</sup>Where x is the concentration in  $\mu\text{g mL}^{-1}$ . <sup>\*\*</sup> n = 5.

$\text{NO}_2:\text{NO}_2^-$  stoichiometric ratio. The colour produced by absorbing a given amount of nitrogen dioxide can also be compared with that produced by adding an equimolar amount of nitrite. The ratio of their absorbance value is known as 'stoichiometric factor'. The  $\text{NO}_2:\text{NO}_2^-$  stoichiometric factor for the proposed method has been evaluated and found to be 0.75, which is in agreement with value in the literature (Table 2, Figure 3). The stoichiometric factor varied and was lowered if sodium arsenite was not used. The following reaction takes place:



Every substance competing with  $\text{NO}_2$  for the  $\text{OH}^-$  will increase the  $\text{NO}_2:\text{NO}_2^-$  stoichiometric factor higher than 0.5.

*Collection efficiency.* The collection efficiency of the absorbing solution was determined by drawing air containing nitrogen dioxide through two impingers connected in series. After sampling, the  $\text{NO}_2$  content of each impinger were analysed separately by the proposed

procedure. It was observed that the first impinger had a collection efficiency of 98-99% at a flow rate of  $0.75 \text{ L min}^{-1}$  whereas the second impinger showed negligible absorbance.

Table 2. Evaluation of  $\text{NO}_2:\text{NO}_2^-$  stoichiometric factor flow rate =  $0.75 \text{ L/min}$ .

No. of analysis	Absorbance due to $\text{NO}_2$ at 420 nm	Absorbance due to $\text{NO}_2^-$ at 420 nm	Stoichiometric factor
1	0.082	0.108	0.759
2	0.140	0.189	0.740
3	0.275	0.362	0.759
4	0.401	0.534	0.750
5	0.529	0.700	0.755
6	0.684	0.884	0.754
7	0.819	1.068	0.758

Mean = 75.35 %.

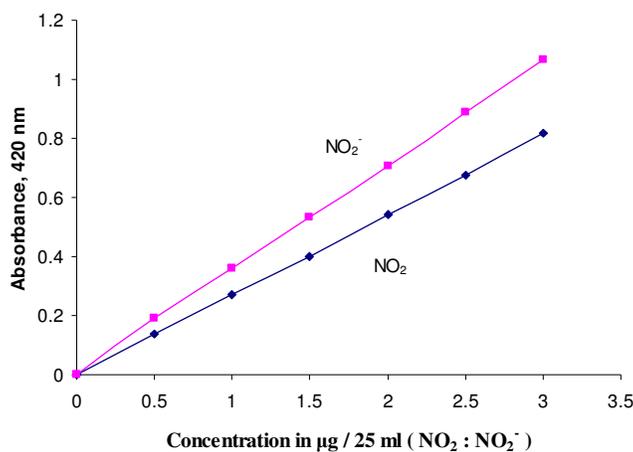


Figure 3.  $\text{NO}_2:\text{NO}_2^-$  stoichiometric ratio.

*Effect of pH.* 1.5-2.0 pH was necessary for complete diazotization. The effect of pH on the absorbance of the dye was studied and found to be 10-11 pH was suitable for full colour development. Above pH 11 the stability and sensitivity of the dye was severely affected.

*Effect of time and temperature.* Diazotization and coupling required 2 minutes for completion. The resulting dye was stable for ~72 hours which makes the method versatile and useful for field measurement. Maximum absorption was obtained by maintaining the absorbing solution at  $4^\circ\text{C}$ .

*Effect of foreign species.* The reliability of the proposed methodology was examined in the presence of possible matrix interferences such as carbon dioxide, ammonia, phenols, aniline, formaldehyde, benzene, xylene and toluene as well as heavy metal ions likely to be present in various samples. Studies were made by adding solution of known amount of these interferences in the absorbing solution before sampling and then analyzed by the proposed method. Heavy metal ions had an appreciable interference on the procedure, which can be masked by adding a 1 mL of 10% EDTA solution.

**Application.** The method has been successfully applied for the determination of nitrogen dioxide in work-room air, cigarette smoke and auto-exhaust and data were compared to those obtained by a reported method (Table 3). In the present method absorbing solution containing 8-hydroxyquinoline and sodium hydroxide is proposed for the collection of nitrogen dioxide. The nitrite formed is diazotized with *p*-nitroquinoline in acidic medium which is subsequently coupled with 8-hydroxyquinoline to give purple azoxine dye in alkaline medium [22].

Table 3. Results of analysis of air.

Source of sample	Volume of sample taken (L) <sup>b</sup>	Nitrogen dioxide found <sup>d</sup>	
		Present method mg/m <sup>3</sup>	Reported method mg/m <sup>3</sup> [22]
Cigarette smoke <sup>c</sup> (with filter)	10	0.24, 0.32	0.22, 0.28
Cigarette smoke (without filter)	10	0.71, 0.65	0.69, 0.61
Auto-exhaust	-	0.38, 0.61	0.41, 0.65
Work-room air	10	0.20, 0.20	0.24, 0.20

<sup>a</sup>Mean of three replicate analyses. <sup>b</sup>Volume of air sample taken – 10 Liters. <sup>c</sup>Smoke of one cigarette analyzed.

### CONCLUSIONS

The proposed method for determining nitrogen dioxide is facile, rapid, sensitive, and has a wide analytical range without the need for extraction or heating. The developed method does not involve any stringent reaction conditions and offers the advantages of high colour stability compared to the other reported method.

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