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Spectrophotometric Determination of Nitrogen dioxide in the Environment

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In the present investigation a simple, sensitive and selective spectrophotometeric method for the determination of nitrogen dioxide in air has been described. The air sample containing nitrogen dioxide is passed through the absorbing solution of acidified potassium iodide to liberate iodine. The liberated iodine bleaches the pinkish-red colour of rhodamine-B dye, which measured at 555 nm. The proposed regent has *ca.* 99 % collection efficiency and stoichiometric ratio of NO_2:NO_2^- is 0.77 Beer's law obeyed over the concentration rage of 0.2-2.0 μg of nitrite/25 mL (0.008-0.08 ppm). The molar absorptivity and Sandell's sensitivity were found to be 5.25×10^5 dm^3 mol^{-1} cm^{-1} and 0.000087 μg cm^{-2}, respectively. The method has been applied for the determination of nitrogen dioxide in autoexhaust and cigarette smoke.

Key Words: Spectrophotometric, Determination, Nitrogen dioxide, Environment.

INTRODUCTION

Several analytical methods are reported for the determination of nitrogen dioxide such as gas chromatography[1], laser induced fluorescence[2], chemiluminescence[3], tunablediode laser[4], liquid chromatography[5], ion chromatography[6], photoaccoustic spectroscopy[7], *etc*. Spectrophotometric methods based on Griess-reaction have also been reported in the literature for the determination of nitrogen dioxide[8]. Many reagents such as *p*-nitroaniline guaicol[9], 8-hydroxy quinoline[10], 1-amino naphthalene-2-sulphonic acid[11], *p*-nitroaniline + α-naphthol[12], N-(1-naphthyl)ethylenediamine, *p*-amino acetophenone and oxalic acid[13]. Potassium iodide and LCV[14], reported from this laboratory, have been useful for the determination of nitrogen dioxide.

The present communication reports a simple and sensitive method for the determination of atmospheric nitrogen dioxide using a pinkish dye rhodamine B. Rhodamine B is a simple and common laboratory reagent. The proposed method is based on the liberation of iodine by the reaction between absorbing solution (KI + HCl) and nitrogen dioxide. The liberated iodine bleaches the pinkish red colour of rhodamine B was having absorption maxima at 555 nm. The proposed reagent (KI + HCl) has *ca.* 99 % collection efficiency. The stoichiometric ratio of NO_2:NO_2^- is 0.77 which is in agreement with values in the literature[15].

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EXPERIMENTAL

All spectral measurements were made with a Toshniwal TVSP-25 spectrophotometer with optically silica cells and a calibrated rotameter (PIMCO) was used for controlling the flow rate while sampling air. A systronics pH meter model 331 was used for pH measurements.

All the chemicals used were of A.R. grade or the best of available quality. Double distilled deionized water used throughout the experiment. Standard sodium nitrite (E. Merck) solution 1 mg mL^{-1} of nitrite and 1 mL of chloroform was added as stabilizer[16]. Working standard of 1 mg $mL^{-1}$of nitrite was prepared daily by appropriate dilution of stock solution. 1 % Aqueous solution of potassium iodide (E. Merck). Rhodamine-B (Stuttgart, W. Germany) solution was prepared 0.02 % (aqueous solution). Absorbing solution was prepared by mixing 7 mL of potassium iodide and 1 mL of HCl (6 M) and diluting the contents to 10 mL with distilled water.

Procedure: Nitrogen dioxide was prepared by bubbling purified air through fresh nitrite solution as described by Nash[17], an aliquot of a solution containing 0.2-2.0 µg of nitrite was taken in an impinger. Nitrogen dioxide was liberated from the aliquot by adding 5 mL of 6 M hydrochloric acid dropwise from a micro-burette. The liberated nitrogen dioxide was absorbed in the absorbing solution taken in two midget impingers of 35 mL capacity each. Containing 10 mL capacity each. Containing 10 mL of the absorbing solution and 0.8 mL of rhodamine B connected to a source of suction. The air was passed through the solution at a rate of 0.75 L/min for 20 min. The solution of the two impinigers were mixed and shaken for 2 min. The volume was made up to 25 mL by adding distilled water. The solution was kept for 15-20 min for the reaction to complete.

Application of the method

In air: Two an air sampling train was fitted in laboratory. In these two impingers containing 10 mL of absorbing solution was connected to a source of suctions. The air was sampled at the rate of 0.75 L/min for 20 min. The aliquots of absorbing solution were then analyzed by the present and reported method[9] Table-1.

In autoexhaust: Nitrogen dioxide presenting autoexhaust was drawn through the two midget impingers each containing 10 mL absorbing solution and attached to an air sampling train. After sampling the absorbing solution were mixed and aliquots were then analyzed by the present method and the reported method[9] Table-1.

In cigarette smoke: Smoke from various brands of cigarettes with and without filter was drawn through three midget impingers connected to an air sampling train. The first two is containing acidic potassium permanaganate (2.5 % $KMnO_4$ w/v in 2.5 % H_2SO_4) for oxidation of nitric oxide (NO) to nitrogen dioxide and third impinger containing 10 mL of the absorbing solution[12]. The cigarette (lighted) was fixed in the glass holder and the air was sucked at the rate of 0.75 L/min. After sampling aliquot was then analyzed by the present and reported method[9] (Table-1).

TABLE-1
DETERMINATION OF NITROGEN DIOXIDE IN VARIOUS AIR SAMPLES

Sample		Total NO_2 found (μg) present method	Reported method[9]
Laboratory air	A	0.66	0.68
(Experimental)	B	0.62	0.60
15 L	C	0.71	0.72
Auto exhaust	A	0.38	0.38
15 L	B	0.37	0.38
	C	0.42	0.40
Cigarette smoke	A	0.44	0.45
With filter	B	0.40	0.44
15 L	C	0.44	0.42
Cigarette smoke	A	0.72	0.67
Without filter	B	0.68	0.68
15 L	C	0.67	0.67

Mean of three replicate analyses.

RESULTS AND DISCUSSION

The absorption spectra of the rhodamine-B showed as maximum absorbance at 555 nm. Beer's law is obeyed over the concentration range 0.2-2.0 μg of nitrite/25 mL (0.008-0.08 ppm). The molar absorptivity ad Sandell's sensitivity were found to be 5.25×10^5 dm^3 mol^{-1} cm^{-1} and 0.000087 μg cm^{-2}, respectively.

The precision of the method was verified by seven replicate analysis of 1 μg of nitrite/25 mL for a period of 7 days. The standard deviation and relative standard deviation were found to be ± 0.0065 and 1.48 %, respectively.

The collection efficiency was determined by passing air containing nitrogen dioxide through two impingers connected in series, each 10 mL of absorbing solution at the rate of 0.75 L/min for 20 min the results show that the proposed reagent has *ca.* 99 % collection efficiency in the first impinger. Stoichiometric factor[18] which is the ratio of absorption of nitrogen dioxide to nitrite is found to be 0.77 by the present method.

10 mL of absorbing solution and 0.8 mL of rhodamine-B were sufficient for bleaching reaction. The solution was kept for 15-20 min for the bleaching reaction. The reaction was carried out at room temperature. All the reactions are carried out at pH 1.5-2.0. The effect of diverse ions commonly found with nitrogen dioxide was studied by adding known amount of diverse ions into the absorbing solution before sampling. Interference from sulphur dioxide and heavy metals was masked with 1 mL of 1 % solution of hydrogen peroxide and EDTA, respectively. Carbon dioxide, ammonia, formaldehyde and phenol, which are present in air with nitrogen dioxide, have no effect on this reaction.

Conclusion

The present method for the determination of nitrogen dioxide is a simple, sensitive and avoids the use of hazardous chemicals. This method can be compared favourable with the reported methods (Table-1). The method can be successfully applied to the trace determination of nitrogen dioxide in laboratory air, autoexhaust and cigarette smoke. Its advantages are mainly due to cheaper cost, easier availability of the reagent.

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