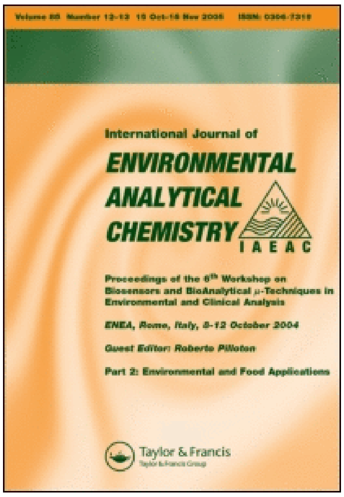

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Báveja, Anil K. and Gupta, V. K.(1983) 'Toxicology of Oxides of Nitrogen and a New Reagent for their Determinaton in Air', International Journal of Environmental Analytical Chemistry, 14: 3, 193 — 200

To link to this Article: DOI: 10.1080/03067318308071619

URL: http://dx.doi.org/10.1080/03067318308071619

Intern. J. Environ. Anal. Chem., 1983, Vol. 14, pp. 193–200
0306-7319/83/1403-0193 $18.50/0

Printed in Great Britain

Toxicology of Oxides of Nitrogen and a New Reagent for their Determination in Air

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(*Received June 8, 1982*)

A new absorbing solution containing α-naphthol in sodium hydroxide is proposed for the collection of nitrogen dioxide. The nitrite formed is diazotized with *p*-nitroaniline in acidic medium which is subsequently coupled with α-naphthol to give purple dye in alkaline medium, which is then extracted in iso-amyl alcohol to give a deep blue colour. The colour reaction is proposed for the extractive spectro-photometric determination of nitrogen dioxide. The collection efficiency and NO_2:NO_2^- stoichiometric factor are evaluated. The method is rapid, simple and free from common interferences and is successfully applied for the analysis of auto exhaust.

KEY WORDS: Nitrogen oxides, air, spectrophotometry.

INTRODUCTION

The oxides of nitrogen are liberated during the use of explosives, in welding operations, in chemical processing involving nitration or the use of nitric acid in various industries, such as dyes, celluloids, etc.[1-3] Higher concentrations up to 1347 ppm and 1200 ppm have been reported to be present in exhaust of internal combustion engines and tobacco smoke respectively.[3] Amongst the oxides of nitrogen, nitrogen dioxide is considered to be the most hazardous because of its acute toxicity. Inhalation of nitrogen dioxide affects mainly the respiratory system, because of its relatively insolubility in water through the relatively dry trachea and bronchii into the moisture filled aveoli of the lungs. On reaching the aveoli the NO_2 is converted to HNO_2 and HNO_3, which are highly irritating and cause acute damage to lungs.[1,3] The nitrous acid formed induces methemoglobineamia as nitrite oxidizes the ferrous state of haemoglobin to ferric state of haemoglobin (methemoglobin) which does not bind oxygen reversibly and death may result due to anoxia in severe cases.[4]

Human studies of both an epidemiologic and toxicologic nature have indicated incidence of bronchitis among infants and school going children.[3] It is also an interesting fact that normal humans exposed to 1 ppm of NO_2 for 24 hrs/day for 180 days developed biochemical altercations including increased chlorestrol lipid and lipo-protein levels.[3] Such a modification suggest a possible relationship to arterioschlerotic actions. Nitrogen dioxide is also reported to cause teratogenic effects.[3] In milder cases of nitrogen dioxide poisoning symptoms such as nausea, vomiting and vertigo with cyanosis may be observed.[5] The presence of nitrogen dioxide is also objectionable because of its vital role in the creation of photochemical smog which cause haze, ozone formation, irritation to living beings and damage to vegetation.[6-9] Though there are differences in opinion on the concentration of nitrogen dioxide required to cause toxic effects, the maximum allowable concentration reported is 5 ppm.[1,9]

The importance of nitrogen dioxide as a pollutant, its detection and determination in air has become vital from the viewpoint of environmental analysis. The spectrophotometric methods reported for the analysis of trace nitrogen dioxide are based on formation of nitrate or nitrite ion in the absorbing medium. The method based on formation of nitrate ion suffer from many disadvantages.[10] The most commonly used methods are that which utilize the formation of nitrite ion and are based principally on the use of Griess type reagents and its modifications. Though a large number of Griess type reagents have been proposed for the determination of nitrite[11] only a few of them are utilized for the determination of atmospheric nitrogen dioxide.[12-14] Jacob and Hochhieser method, the most widely used method, suffers from rigorous control of pH and relatively larger time for full colour development and low collection efficiency.[12] Recently we have reported a rapid, selective and sensitive method for the determination of nitrite using *p*-nitroaniline and α-naphthol.[15] The method is further modified to determine atmospheric nitrogen dioxide by using a new absorbing solution containing α-naphthol in sodium hydroxide. The blue coloured iso-amyl alcohol extract of the dye shows a maximum absorption at 610 nm. Beer's law range is 1 to 8 μg of NO_2^- per 10 ml extract. The molar absorptivity and Sandell's sensitivity are 5.24×10^4 l.mole^{-1} cm^{-1} and 0.00088 μg cm^{-2}. The collection efficiency of the absorbing solution and NO_2:NO_2^- stoichiometric ratio were found to be 96% to 98% and 0.74 respectively. Other reaction parameters have also been evaluated.

EXPERIMENTAL

Apparatus

ECIL spectrophotometer model GS 865 and Carl Zeiss Spekol with 1 cm matched glass cells were used for all spectral measurements. Fritted midget impingers (frit. dia ~ 10 mm) of 35 ml capacity were used for air sampling. Flow rate adjustable calibrated rotameters were used for measuring the air flow.

Reagents

A standard sodium nitrite containing 4 μg of NO_2^- per ml was prepared for plotting the calibration curve. A 1×10^{-3} M solution of precrystallized *p*-nitroaniline in 2 N hydrochloric acid and 2 N aqueous sodium hydroxide solutions were also prepared.

Absorbing solution

The absorbing solution was prepared by dissolving 100 mg of α-naphthol in 100 ml of 0.1 N sodium hydroxide containing 2.5 ml of ethanol.

Nitrogen dioxide was prepared by bubbling air through fresh nitrite buffer and acidic potassium permanganate as reported by Nash.[16]

All reagents used were on AnalaR grade.

Procedure

Air is sampled through a 10 ml absorbing solution taken in the midget impinger at a rate of 0.75 litres/min. After sampling the absorbing solution was quantitatively transferred to a 125 ml pear shaped separatory funnel and diluted to 50 ml. 1.5 ml of *p*-nitroaniline was added and the acidity was adjusted to 0.5 M with hydrochloric acid. The solution was shaken for two minutes and made alkaline with excess of 2 M sodium hydroxide. The dye formed was extracted in 10 ml of iso-amyl alcohol by taking two aliquots of 5 ml. The absorbance of blue coloured dye was measured at 610 nm against a reagent blank. The amount of nitrogen dioxide was calculated from a calibration curve prepared from a standard sodium nitrite solution containing 1 to 8 μg NO_2^-/50 ml after correcting with stoichiometric factor (Table I). For samples of higher concentrations of nitrogen dioxide, aliquots of the absorbing solution were used. Interferences from heavy metals and sulphur dioxide were masked by EDTA and H_2O_2 prior to the addition of sodium hydroxide.

TABLE I
Calibration data for determination of nitrogen dioxide

NO_2 µg/10 ml of iso amyl extract	Absorbance[a] 610
1	0.085
2	0.170
3	0.225
4	0.340
5	0.425
6	0.510
7	0.595
8	0.680

[a] Absorbance was calculated by multiplying the absorbance value of nitrite ion concentration (extracted from 50 ml of water) with 0.74 (stoichiometric factor).

RESULTS AND DISCUSSION

The method reported here is simple, rapid and sensitive ($\varepsilon = 5.24 \times 10^4$ $\text{l.mole}^{-1}\text{cm}^{-1}$ computed from NO_2^- concentrations). After sampling only 10–15 min. are required for full colour development. The blue dye extract has an absorption maxima at 610 nm and the dye formed is stable for ≥ 30 hours. Lower concentrations of nitrogen dioxide can also be determined thus making the method sensitive, versatile and useful for field measurements. The collection efficiency, optimal flow rate for collection efficiency, the stoichiometric factor, interferences have been studied.

The collection efficiency

The collection efficiency of the absorbing solution was determined by drawing nitrogen dioxide containing air through two impingers connected in series as proposed by Jacobs and Hochhieser.[12] After sampling the NO_2 contents of each impinger were analysed separately by the recommended procedure. Collection efficiency was computed from the data obtained. The results in Table II show that the first impinger has a collection efficiency of 96–98.2% at a flow rate of 0.75 litres/min. A study was also carried out to see the effect of the flow rate on the collection efficiency. The results in Table III show that the collection efficiency of the first impinger decreases with the increase in flow rate. Triethanolamine and guaiacol as recommended by Huygen and Steerman[17] and Nash[16]

TABLE II

Collection efficiency of absorbing solution
Flow rate $=0.75$ litre/min

No. of analysis[a]	NO_2 absorbed in first impinger µg	NO_2 carried over[b] µg	Total NO_2 µg	Collection efficiency of first impinger %
1	1.85	0.05	1.90	97.3
2	2.65	0.10	2.75	96.3
3	4.95	0.20	5.15	96.1
4	6.80	0.20	7.00	97.1
5	8.65	0.15	8.80	98.2
6	10.35	0.20	10.55	98.1
7	14.95	0.55	15.50	96.4
8	16.70	0.45	17.15	97.3

[a] Different amounts of NO_2 were produced by changing the strength of nitrite buffer.
[b] Measurements were made after extracting with 2 ml of iso-amyl alcohol.

TABLE III

Effect of flow rate on collection efficiency

Flow rate lit/min	NO_2 absorbed in first impinger µg	NO_2 carried over µg	Total amount of NO_2 µg	Collection efficiency %
0.50	13.80	0.35	14.15	97.50
	14.30	0.30	14.60	97.90
0.75	11.85	0.21	12.06	98.20
	8.65	0.15	8.80	98.20
	20.16	0.36	20.52	98.15
1.00	9.45	0.50	9.95	95.45
	12.60	0.67	13.27	94.90
1.50	16.50	1.42	17.91	92.10
	18.25	2.21	20.46	89.19
2.00	17.00	4.00	21.00	80.95
	14.00	3.68	17.68	79.18
4.00	15.52	13.98	29.50	52.60
	10.18	10.34	20.52	49.61

were found to be unsuitable for enhancing the collection efficiency as they interfered with the method.

NO_2: NO_2^- stoichiometric factor

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 is known as the stoichiometric factor or sometimes referred as "Saltzman Factor".[13] This NO_2:NO_2^- stoichiometric factor was evaluated by the procedure of Nash.[16] In our experiment we replaced Arnold tubes by fritted midget impingers. A factor ranging from 0.72 to 0.75 was obtained for five concentrations by the present method. We propose the mean value of 0.74 as the stoichiometric factor for this method. No difference in the factor was observed even if sodium arsenite was used, as reported.[18] Results in Table IV.

TABLE IV

Evaluation of NO_2: NO_2^- stoichiometric factor

No. of analysis	Absorbance due to NO_2[a] 610 nm	Absorbance due to NO_2^-[b] 610 nm	Stoichiometric factor
1	0.215	0.285	0.754
2	0.270	0.360	0.750
3	0.370	0.510	0.725
4	0.420	0.570	0.737
5	0.595	0.800	0.743
		Mean ≈	0.741

[a] NO_2 was absorbed in absorbing solution after passing nitrous acid vapour through acidic $KMnO_4$.
[b] Nitrous acid vapour was absorbed in NaOH.

Interferences

It was shown that the interference from sulphur dioxide and heavy metals can be masked with H_2O_2 and EDTA respectively.[15] The interference due to ozone if present can be eliminated by exposing the air stream to rubber which reacts with ozone and not with nitrogen dioxide.[19] CO, NH_3, phenol, aniline and formaldehyde which are commonly associated with nitrogen dioxide, have no effect on the colour development.

Application of the method in analysis of air and auto exhaust

The method has been successfully applied for analysing nitrogen dioxide in various samples. Three types of samples were analysed, viz. NO_2 produced by nitrite buffer/$KMnO_4$, NO_2 in air and NO_2 in scooter exhaust. In each case the sampled air was divided into two parts each having a flow rate of 0.75 l/min. One part was analysed by the procedure given in the proposed method and the other according to Nash.[16] The results obtained are in full agreement with each other (Table V).

TABLE V

Analysis of samples containing nitrogen dioxide

Source of sample	Volume of sample taken (litres)	Nitrogen dioxide found Present method μg	 Nash's method μg
Nitrite buffer/	10	3.1	2.7
	40	9.6	9.4
	60	14.8	14.9
	120	21.4	22.6
Air	100	7.6	7.8
	150	9.2	8.7
	200	13.1	13.4
Scooter exhaust	7.5	4.1	4.0
	22.5	10.6	10.8

The method proposed is rapid and free from rigorous control of experimental conditions. The higher collection efficiency and stability of the colour are added advantages. The reagents are stable and easily obtainable. The method can be used for routine analysis of nitrogen dioxide in air as well as auto exhaust, without special modifications.

Acknowledgements

The authors are thankful to Prof. S. G. Tandon, Head, Department of Chemistry, Ravishankar University, Raipur for providing necessary laboratory facilities. One of them (AKB) is thankful to CSIR, New Delhi for award of Research Fellowship.

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