

New Spectrophotometric Method for Determining Nitrogen Dioxide in Air Using 2,2-azino-bis(3-ethyl benzothiazoline)-6-Sulfonic Acid-Diammonium Salt and Passive Sampling

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Abstract: A new simple and highly sensitive spectrophotometric method for determining nitrogen dioxide in air was developed. The method is based on converting atmospheric nitrogen dioxide to nitrite ions within the IVL passive samplers used for samples collection. Acidifying nitrite ions with concentrated HCl produced the peroxy-nitrous acid oxidizing agent which was measured using 2,2-azino-bis(3-ethyl benzothiazoline)-6-sulfonic acid-diammonium salt (ABTS) as reducing coloring agent. A parallel series of collected samples were measured for its nitrite content using a validated ion chromatographic method.

The results obtained using both methods were compared in terms of their sensitivity and accuracy. Developed spectrophotometric method was shown to be one order of magnitude higher in sensitivity compared to the ion chromatographic method. Quantitation limits of 0.05 ppm and 0.55 $\mu\text{g}/\text{m}^3$ were obtained for nitrite ion and nitrogen dioxide, respectively. Standard deviations in the ranges of 0.05–0.59 and 0.63–7.92 with averages of 0.27 and 3.11 were obtained for determining nitrite and nitrogen dioxide, respectively.

Student-t test revealed t-values less than 6.93 and 4.40 for nitrite ions and nitrogen dioxide, respectively. These values indicated insignificant difference between the averages of the newly developed method and the values obtained by ion chromatography at 95% confidence level.

Compared to continuous monitoring techniques, the newly developed method has shown simple, accurate, sensitive, inexpensive and reliable for long term monitoring of nitrogen dioxide in ambient air.

Keywords: spectrophotometry, nitrogen dioxide, nitrous acid, peroxy-nitrous acid, atmosphere, ABTS, passive samplers, ion chromatography

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1. Introduction

Several analytical methods have been used for nitrite trace analysis. Many spectrophotometric methods are based on formation of colored azodyes that can be measured at certain wavelengths.¹ Other methods include kinetic,^{2,3} chromatography,^{4,5} potentiometry,^{6,7} amperometry,⁸ polarography,⁹ capillary electrophoresis,¹⁰ spectrophotometry^{11,12} and flow injection analysis (FIA)^{13–16} have also been reported. Some of these reported methods have the disadvantages of being time consuming and serious interferences.

ABTS is a redox coloring reagent that has been used for enzymatic peroxide tests,¹⁷ percarboxylic acid analysis¹⁸ and selective determination of reactive bromine and chlorine species.¹⁹ Oxidation of ABTS undergoes two e-electron transfer steps giving rise to ABTS^{•+} and ABTS⁺⁺ as stable green and violet colored radicals that have broad absorbance spectra with several maxima and high molar absorptivities at 415, 650, 728, and 815 nm.²⁰ These radicals were obtained in enzymatic oxidizing of ABTS using myoglobin²¹ or horseradish peroxidase²² and in chemical oxidation using MnO₂,²³ potassium persulfate,²⁴ peroxide radicals²⁵ or electrochemically.²⁶

On the other hand, passive sampling involve sampling a specific gas pollutant or vapor from the atmosphere at a rate controlled by diffusion through a static air layer or permeation through a membrane.²⁷ Passive sampling methods are characterized by being of low cost, low technical demand as well as expediency for monitoring many polluted locations.^{28,29}

The aim of this study is to develop a new method for measuring low concentrations of nitrogen dioxide in the atmosphere. The method is based on extracting NO₂ from air as nitrite using the passive sampling technique. Nitrite ions extracted will be subsequently acidified and measured using 2,2-azino-bis(3-ethyl benzothiazoline)-6-sulfonic acid-diammonium salt (ABTS) as oxidation-reduction coloring reagent. The results obtained will be compared with ion chromatographic measurements on the same samples batches.

2. Experimental

2.1. Materials

Reagent grade chemicals and deionized water were used throughout. 2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid-diammonium salt reagent (ABTS) was purchased from Sigma-Aldrich. Hydrochloric acid

and sodium nitrite were purchased from Merck. IVL passive sampler was purchased from the Swedish Environmental Research Institute (IVL).

2.2. Standard solutions

A stock (10⁻³ M) standard solution of ABTS was prepared by dissolving 0.0548 g of diammonium-ABTS salt in 100.0 ml of deionized water and stored at 4 °C.

A 10.0 ppm standard solution of sodium nitrite into 100.0 ml of deionized water was prepared as usual. A 0.1 M hydrochloric acid solution into 1.0 L of deionized water was prepared and standardized as usual.

Impregnation solution for the passive samplers' filters was prepared by dissolving 7.90 g of NaI and 0.88 g of NaOH into 100.0 ml methanol. The mixture was shaken well in ultrasonic bath.

A 10⁻³ M Triethanolamine as nitrite ions extracting solution was prepared by transferring 13.3 µl of triethanolamine to a 100.0 ml volumetric flask. The solution was made to 100.0 ml using deionized water.

2.3. Apparatus

Absorption measurements were performed using Cary-50 UV-Vis spectrophotometer (Varian, Inc., Austria) with 1.0 cm quartz cells.

IVL passive samplers developed by the Swedish Environmental Research Institute were used to collect nitrogen dioxide from air. A sampler consists of bottom led impregnation filter, passive sampler tube, Teflon filter, steel net and front led as shown in Figure 1.

Samplers were mounted on a shielding plate with their open sides oriented downwards to protect them from direct exposure to sunlight, wind, dust fall and rain. Exposure time periods of fourteen days were applied for all samplers and then transferred to the lab for analyzing.

An ICS-90 ion chromatograph, Dionex Corp., USA, supported with an AS9-SC anion analytical column and anion Micro Membrane Suppressor (AMMS) was also used for measuring nitrite ions concentrations in the same samples batches.

2.4. Procedures

2.4.1. Optimization of the spectrophotometric method

Several experiments were conducted to establish the optimum conditions for the reaction between nitrite

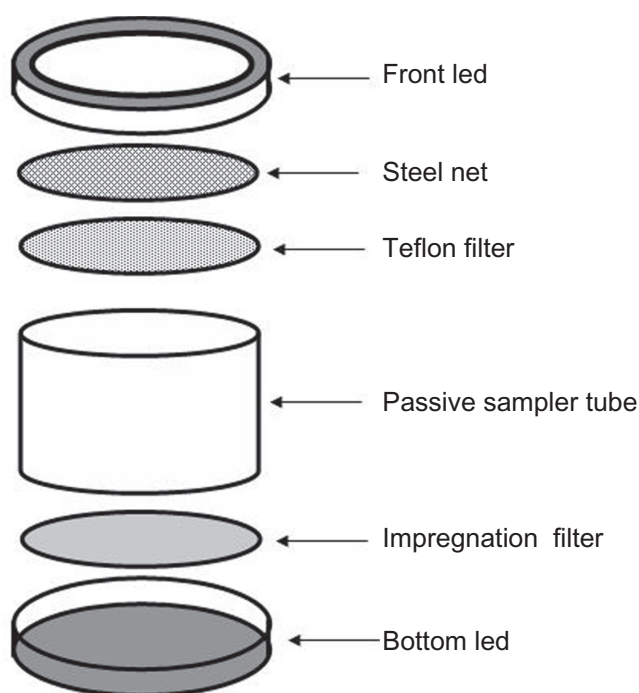


Figure 1. Components of the IVL passive sampler.

ions and ABTS. Variables such as time, concentrations of HCl, ABTS and nitrite and the order of reagents' addition were investigated. Stoichiometry of the reaction between nitrite and ABTS was also studied.

2.4.1.1. Effect of time

The effect of time on the rate of ABTS oxidation was studied by mixing 1.0 ml of 10^{-3} M ABTS with 3.0 ml of 0.1 M HCl and 1.0 ml of 5.0 ppm nitrite solution into 10.0 ml volumetric flask. The solution was made up to 10.0 ml using deionized water and its absorption spectra were scanned at three minutes time intervals in the wavelength range 200–500 nm.

2.4.1.2. Effect of HCl concentration

The concentration of HCl needed to oxidize ABTS at convenient reaction rate was studied. Into 10.0 ml volumetric flasks, 1.0 ml portions of the 10^{-3} M ABTS were mixed with 1.0 ml of the 10.0 ppm nitrite solution each. A 1.0 ml of (0.001–1 M) standard HCl solution was added to each flask.

In another experiment, volumes of 0.5–8 ml of 0.1 M HCl solution were added to 10.0 ml volumetric flasks containing 1.0 ml of the 10^{-3} M ABTS mixed with 1.0 ml of the 10.0 ppm nitrite solution. The total volume was made up to 10.0 ml and their absorption

spectra were scanned in the wavelength range 200–500 nm.

2.4.1.3. Effect of addition order

The effect of addition order of HCl, ABTS and nitrite ions on the reaction rate was studied. A mixture of 1.0 ml of 10^{-3} M ABTS, 3.0 ml of 0.1 M HCl and 1.0 ml of 5.0 ppm nitrite ions was prepared several times by inverting the order of addition. Resulted solutions were made up to 10.0 ml into volumetric flask. Solutions were incubated for 2.0 minutes at room temperature and scanned in the wavelength range 200–500 nm.

2.4.1.4. Calibration curve

Into 10.0 ml volumetric flasks, 50–600 μ l portions of the 10.0 ppm standard nitrite ions were added to mixtures of 3.0 ml of 0.1 M HCl and 1.0 ml of 10^{-3} M ABTS and made up to 10.0 ml using deionized water. Resulted solutions were incubated for 2.0 minutes at room temperature and their absorbencies at 415 nm against blank containing all ingredients except nitrite ions were measured. Nitrite concentrations in the range of 0.05–0.6 ppm were obtained. Calibration graph of absorbance versus concentration of nitrite ion was plotted.

2.4.2. Sampling of nitrogen dioxide from air (real samples)

The filter paper placed into the sampler's bottom led was impregnated by 50 μ l of the impregnation solution and left to dry for ten minutes. Samplers were then assembled and mounted for fourteen days in selected locations of the city. Nitrogen dioxide in atmosphere was converted into nitrite on the sampler filters. The filters were removed then placed in 10.0 ml vials and soaked into 5.0 ml of the extracting solution. Triethanolamine in extracting solution reduces the iodine formed on the sampler due to the reaction of iodide from the impregnation solution with nitrogen dioxide from air. Vials were closed and shaken carefully to ensure full extraction of all nitrite ions from the filters into the solution.

A 0.7 ml of each nitrite solution produced was mixed with 3.0 ml of 0.1 M hydrochloric acid and 1.0 ml of 10^{-3} M ABTS. The solution was made up to 10.0 ml by deionized water. Resultant solution was incubated for two minutes at room temperature and its absorbance at 415 nm was recorded. The analysis was



repeated at least three times for each sample and the average result was calculated.

A blank sampler treated in the same way, was mounted in the laboratory during the sampling period and analyzed in the same way.

2.4.3. Ion chromatography

Nitrite ions concentrations were measured using AS9-SC anion column on the Dionex ICS-90 ion chromatograph. Anion Micro-Membrane suppressor (AMMS) and dilute sulfuric acid for re-generation were used. A 1.8×10^{-3} M sodium carbonate was used as eluent. Standard nitrite solutions, ranging from 1–20 ppm, were prepared using the stock standard solution (100.0 ppm) purchased from Dionex. Calibration graph was prepared by plotting the area integration of the nitrite peak versus the concentration of standard samples. Nitrite ions extracted from the passive samplers were measured under the same condition.

2.4.4. Calculations of the NO_2 concentration in air
Concentration of nitrogen dioxide (NO_2) in air was calculated using the following formula equation given by IVL protocol.^{30–32}

$$C_{(\text{NO}_2)} = \frac{m(\text{NO}_2^-)\nu}{0.0323t}$$

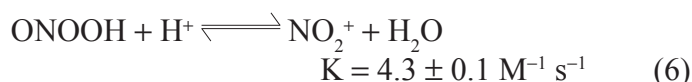
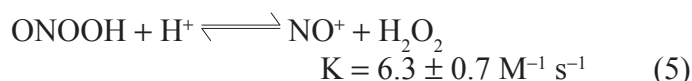
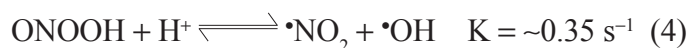
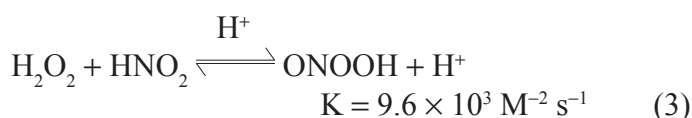
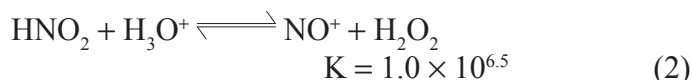
where $C_{(\text{NO}_2)}$ is the concentration of the sampled gas in units of $\mu\text{g NO}_2/\text{m}^3$, $m(\text{NO}_2^-)$ is the concentration of NO_2^- determined in the extract from the filter in the unit of $\mu\text{g}/\text{ml}$, ν is the extraction volume of the filter and equals 5 ml for the IVL samplers used, t is the time of exposure in days (ie, 24 h units) and 0.0323 is the sampler uptake rate for NO_2 which has the unit of m^3/day .

3. Results and Discussion

3.1. Nitrite decomposition in aqueous acidic solutions

Nitrite ions in acid solution readily form nitrous acid (HNO_2) with rate constant of $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (reaction 1).³³ Nitrous acid in strongly acidic solution rapidly dissociates into the active electrophile nitrosonium ion (NO^+) and hydrogen peroxide (reaction 2). The life time of NO^+ in water is very short ($\sim 3 \times 10^{-10}$ s) and is only found at high acidity.³⁴ This leads to the accumulation of H_2O_2 in solution which reacts with

HNO_2 to produce peroxyntrous acid (ONOOH) whose pK_a is in the range of 6.5–6.8 (reaction 3).³⁵ Although the rate constant for reaction 5 is approximately 50% higher than reaction 6, accumulation of NO^+ from reaction 2 will shift the former to the backward. Consequently reaction 6 will dominant.³⁵



H^+ catalyzed decomposition of ONOOH at $\text{pH} < 2$ (in our case) is the dominant mechanism with a decay rate linearly proportional to $[\text{H}^+]$. Due to the differences in the rate constants, decomposition/homolysis of ONOOH will give different oxidant species in solution; namely $\cdot\text{OH}$, $\cdot\text{NO}_2$, NO_2^+ , NO^+ and H_2O_2 (reactions 4–6).³⁶

Peroxyntrite ion (ONOO^-) is a relatively stable species having a maximum absorption at 302 nm with $\epsilon = 1670 \pm 50 \text{ M}^{-1} \text{ cm}^{-1}$,³⁷ whereas ONOOH is less stable with maximum absorption at 240 nm and $\epsilon = 770 \text{ M}^{-1} \text{ cm}^{-1}$. No appreciable absorption was observed above 300 nm for both species.³⁸

ONOOH indirectly oxidizes substrates via the highly oxidizing species formed during its decomposition such as $\cdot\text{NO}_2$ and $\cdot\text{OH}$ radicals. It also fast reacts directly with some substrates such as sulfhydryls,³⁹ metal complexes,⁴⁰ ebselen,⁴¹ iron,⁴² manganese⁴³ porphyrins, heme proteins⁴⁴ and ABTS.⁴⁵ Reducing substances such as ebselen and iron(III) porphyrin were assumed to scavenge ONOOH before being isomerized. This is because ONOOH oxidizes substrate with the same rate as its isomerization.^{46,47}

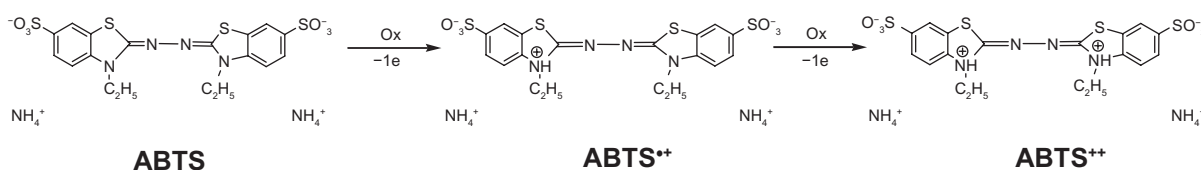


Figure 2. Two electron oxidation steps of ABTS (2,2-azino-bis(3-ethylbenzothiazoline)-6-sulfonate) to ABTS^{•+} and ABTS⁺⁺.

Rate constants of $2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $2.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ were reported for ebselen⁴⁸ and iron(III) porphyrin,⁴¹ respectively.

3.2. Absorption spectra of ABTS^{•+}

In our developed method, oxidation of 2,2-azino-bis(3-ethyl benzothiazoline)-6-sulfonic acid-diammonium salt (ABTS) by peroxyxynitrous acid or its decomposition products gave the oxidized form of (ABTS^{•+}). ABTS^{•+} has a green-blue color, which absorbs strongly at 415 nm. The reaction is going in two electrons oxidation process as follows:

Figure 3 shows the UV-VIS absorption spectra of 1.0 ml of 10^{-3} M ABTS after successive additions of different volumes of standard nitrite solution to produce concentrations of 0.1–0.6 ppm. The broad intense band at 315 nm is attributed to the reduced form of ABTS. This band was not shown when ABTS totally existed in the reduced form. Upon conversion to the oxidized form (ABTS^{•+}), spectra showed broad intense bands at 415 nm. This strong band corresponds to the half oxidation of ABTS to ABTS^{•+} has been used for monitoring nitrite ions concentration in solution throughout our investigation. Figure 3 shows

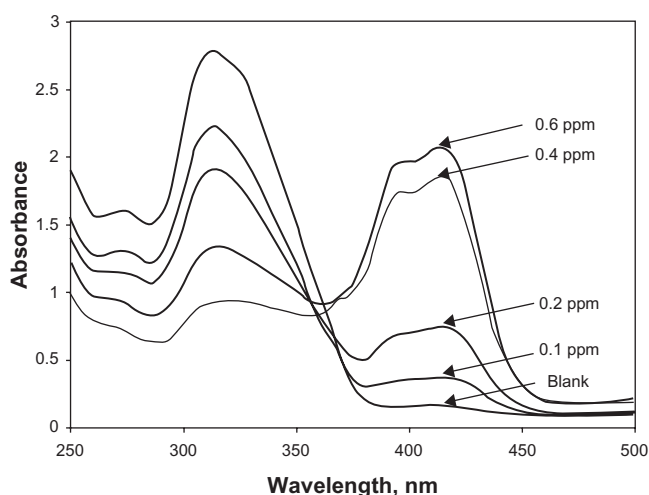


Figure 3. Absorption spectra of 1.0 ml of the 10^{-3} M ABTS at different concentrations (0.1–0.6 ppm) of nitrite.

that by increasing nitrite concentration, the intensity of the 315 nm band decreased while that of 415 nm band increased. An isoesbetic point around 360 nm was obtained indicating a reversible redox reaction at equilibrium.

Other previously reported bands at 650, 732 and 820 nm were not shown since they are produced by the fully oxidized species (ABTS⁺⁺) which was not formed in our study.⁴⁹

Therefore the increase in absorbance at 415 nm was used for measuring the change in nitrite ion concentration of nitrite in our collected samples.

3.3. Effect of hydrochloric acid

The effect of HCl concentration on the reaction rate was studied by adding 0.5–3 ml of 0.1 M standard HCl solution to 1.0 ml of 10^{-3} M ABTS mixed with 1.0 ml of 10 ppm nitrite solution and the total volume was made up to 10 ml by deionized water. Solutions were incubated for two minutes at room temperature and their UV-Vis spectra were scanned. The rate of reaction was found to increase with increasing HCl concentration as shown in Figure 4. After several experiments, 3.0 ml of 0.1 M. HCl showed nearly the complete conversion of 1.0 ml of 10^{-3} M ABTS to ABTS^{•+}. Therefore all subsequent measurements were made using 3 ml of 0.1 M HCl.

3.4. Effect of time

Figure 5 shows the effect of time on the reaction rate of 1.0 ml of 10^{-3} M ABTS mixed with 3.0 ml of 0.1 M HCl and 1.0 ml of 5.0 ppm nitrite. A slow reaction that needs long time to be terminated was observed. Calibration curves at different incubation time intervals were plotted and used for checking concentrations of standard nitrite samples. Two minutes incubation time gave the best linear regression and recoveries. The reason can be attributed to a change in the kinetic order of the reaction by time. Therefore, two minutes incubation time was used in our all subsequent measurements.

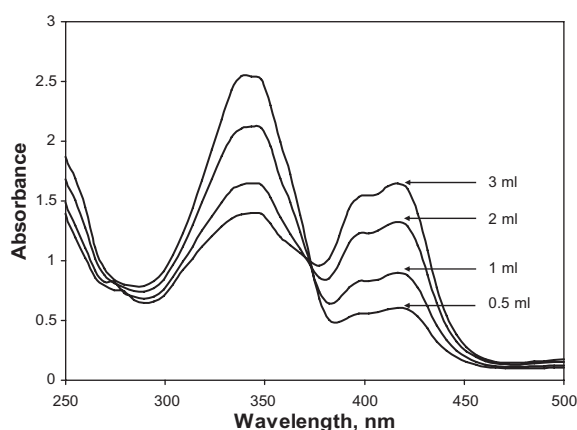


Figure 4. Effects of HCl concentration on the reaction of 1.0 ml of 10^{-3} M ABTS mixed with 1.0 ml of 10 ppm nitrite solution into 10.0 ml volumetric flasks. 0.5–3 ml of 0.1 M standard HCl solution was added. The total volume was adjusted to 10.0 ml in each flask.

3.5. Effect of order of addition

Addition order was studied by mixing 3.0 ml of 0.1 M HCl with 1.0 ml of 5.0 ppm nitrite solution and 1.0 ml of 10^{-3} M ABTS as mentioned in section 2.4.1.3. The mixture was incubated for two minutes and its absorbance was measured at 415 nm. Addition order was inverted and absorbance was measured similarly. The results showed that the reaction between ABTS and nitrite in strong acidic solution is not affected by the addition order of reagents.

3.6. Calibration and sensitivity

Figure 5 shows the calibration plot of nitrite concentration in ppm versus absorbance at 415 nm. Straight line in the dynamic range of 0.05–0.6 $\mu\text{g}/\text{ml}$ with linear regression of $Y = 1.271 X + 0.032$ was obtained. Correlation coefficient, $R^2 = 0.998$, and slope of 1.271

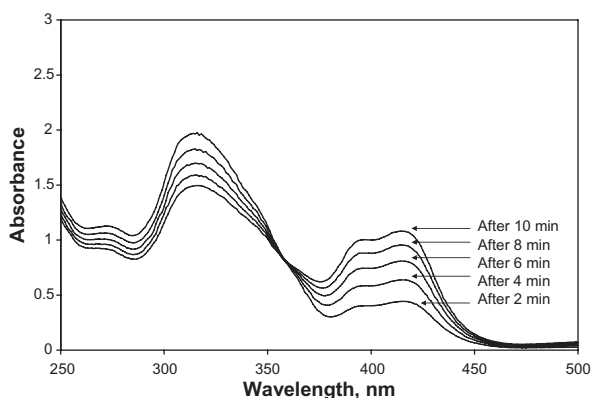


Figure 5. Effect of time on reaction rate of 1.0 ml of 10^{-3} M ABTS mixed with 3.0 ml of 0.1 M HCl and 1 ml of 5.0 ppm nitrite solution. The mixture was made to 10.0 ml by deionized water in volumetric flask. The absorption spectra were scanned at 2 minutes time intervals.

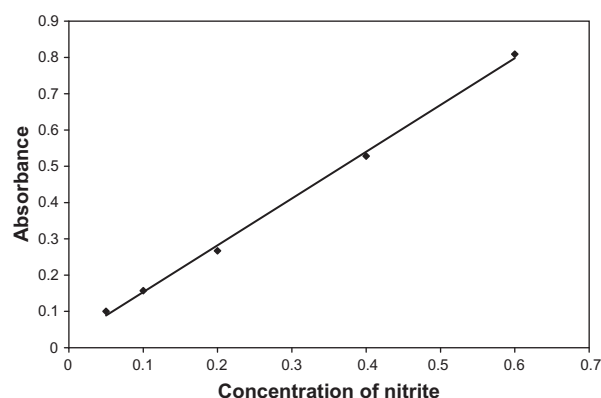
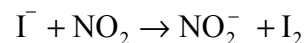


Figure 6. Calibration curve of nitrite concentration in ppm versus absorbance. Successive amounts of nitrite solution were added to 3 ml of 0.1 M HCl and 1 ml of 10^{-3} M ABTS. The solution was made up to 10.0 ml by deionized water.

were obtained. Quantitation limit of 0.05 ppm indicates high sensitivity for measuring low concentration of nitrite was also obtained. This limit is far less than the quantitation limits of spectrophotometric fluorimetric and electrochemical methods for measuring nitrite in water, food, saliva, urine previously published.⁵⁰ This limit also reflects a $0.55 \mu\text{g}/\text{m}^3$ as quantitation limit for determining nitrogen dioxide in atmosphere.

3.7. Application to real samples

To test the validity of developed spectrophotometric method in measuring nitrogen dioxide in air, a number of passive samplers were distributed in different locations of the city over the months May, June, July and September. Samplers were collected after fourteen days exposure. Nitrogen dioxide in air diffused through the filter was converted into nitrite by reaction with iodide and then extracted into deionized water.



Nitrite contents were subjected to determination using the developed and the ion chromatographic methods. The results obtained are shown in Table 1. A good agreement between results obtained for nitrite and nitrogen dioxide contents by both methods were obtained. Standard deviations of 0.05–0.59 and 0.63–7.92 for determining nitrite and nitrogen dioxide were respectively obtained.

Applying student-t test for the results obtained by both methods gave t-values less than 6.93 and 4.40 for nitrite ions and nitrogen dioxide, indicating

Table 1. Nitrite ion and nitrogen dioxide concentrations of some air samples using the newly developed spectrophotometric method and the ion chromatographic method.

No.	Season	Average ppm concentrations of nitrite ions		Average $\mu\text{g}/\text{m}^3$ concentrations of nitrogen dioxide in air		t-value	t-value			
		Average absorbance	Spectrophotometric method	SD**	Ion chromatogr. method			Spectrophotometric method	SD**	Ion chromatogr. method
1	May	0.557	5.90	0.23	5.18	5.38	65.24	3.14	57.28	4.40
2	May	0.287	2.87	0.18	3.29	4.04	31.70	2.44	36.38	3.32
3	May	0.323	3.27	0.59	3.35	0.24	36.19	7.92	37.04	0.19
4	June	0.635	6.76	0.08	6.44	6.93	74.69	2.96	71.21	2.04
5	June	0.418	4.33	0.22	3.8	4.09	47.91	3.03	42.02	3.36
6	July	0.224	2.15	0.10	1.34	11.90	23.81	1.24	14.82	-
7	July	0.135	1.16	0.07	ND*	-	12.83	0.96	ND*	-
8	July	0.434	4.52	0.28	4.6	0.50	49.98	3.78	50.86	0.40
9	July	0.530	5.60	0.37	5.83	1.09	61.92	4.97	64.46	0.88
10	Sept.	0.297	2.97	0.05	3.05	3.01	32.88	0.63	33.72	2.31

Notes: *ND, not detected; **SD, standard deviation was calculated based on at least three determinations.

insignificant difference in accuracy between the average of the newly developed spectrophotometric method and the ion chromatographic method at 95% confidence level.

Since the concentration range of the developed method is less than the ion chromatographic method (0.05–0.6 $\mu\text{g}/\text{ml}$), samples were diluted before spectrophotometric measurements.

4. Conclusion

A new highly sensitive spectrophotometric method to measure low concentrations of nitrogen dioxide in ambient atmosphere was developed. The method is based on converting NO_2 to nitrite ions within the IVL passive samplers used for samples collection. Resultant nitrite ions were rapidly converted to peroxyxynitrous acid by addition of concentrated HCl. Peroxyxynitrous acid was calorimetrically measured using ABTS as reducing agent. The latter was converted into ABTS^+ which absorbed maximally at 415 nm. For comparison, collected samples were measured for its nitrite contents using a validated ion chromatographic method.

Developed new spectrophotometric method has shown to be one order of magnitude higher in sensitivity compared to the ion chromatographic method. Quantitation limits of 0.05 ppm and 0.55 $\mu\text{g}/\text{m}^3$ were obtained for nitrite ion and nitrogen dioxide, respectively. Standard deviations in the ranges of 0.05–0.59 and 0.63–7.92 with averages of 0.27 and 3.11 were obtained for determining nitrite and nitrogen dioxide, respectively.

The quantitation limit of 0.05 ppm nitrite ions obtained by developed method is less than some quantitation limits obtained by spectrophotometric, fluorimetric and electrochemical methods previously reported for measuring nitrite ions in water, food, saliva and urine.⁵⁰

Student-t test revealed t-values less than 6.93 and 4.40 for nitrite ions and nitrogen dioxide, respectively. These values revealed insignificant difference between the average values determined by the newly developed method and values obtained by the validated ion chromatographic method at the 95% confidence level. Compared to continuous monitoring techniques, the newly developed method has shown simple, accurate, sensitive, inexpensive and reliable for long time monitoring of nitrogen dioxide in air.



Disclosure

This manuscript has been read and approved by all authors. This paper is unique and is not under consideration by any other publication and has not been published elsewhere. The authors and peer reviewers of this paper report no conflicts of interest. The authors confirm that they have permission to reproduce any copyrighted material.

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