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Spectrophotometric determination of nitrogen dioxide, nitrite and nitrate with Neutral Red

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Abstract. A simple and sensitive spectrophotometric method for the determination of nitrogen dioxide in air and nitrite in water, soil, some analytical grade chemicals and tooth paste has been developed. Nitrogen dioxide in air is fixed as nitrite ion in alkaline sodium arsenite or triethanolamine absorber solution. The method is based on the reaction of nitrite in aqueous medium with known excess of Neutral Red (C.I. 50040), an azine dye having a primary amino group with absorption maxima at 530 nm. In acid medium, it showed a decrease in colour intensity due to diazotization, followed by deamination. Addition of bromide ion enhances the rate of diazotization, and the reaction goes to completion almost instantaneously. Beer's law is obeyed over the range 0 – 20 µg nitrite and the molar absorptivity is $2.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. The colour system is stable for 2 days. The dye can be extracted under alkaline condition in iso-amyl alcohol and the addition of methanolic sulphuric acid restores the dye colour. It showed molar absorptivity of $4.3 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. Beer's law is obeyed over the range 0 – 1.6 µg of nitrite, having a detection limit of 0.15 µg.

Key words. Neutral Red – nitrogen dioxide – nitrite – nitrate – solvent extraction.

Introduction

Nitrogen dioxide is the most hazardous pollutant among the oxides of nitrogen and plays an important role in the for-

mation of acid rain [1], photochemical smog and in generation of many secondary pollutants [2]. Maximum admissible concentration of nitrate and nitrite in drinking water being 50 and 0.1 mg L⁻¹ respectively [3].

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Various instrumental methods such as polarography [4], voltammetry [5], fluorimetry [6], biamperometry [7] and flow injection spectrophotometry [8] have been used for nitrite determination. Nitrite is determined spectrophotometrically based on diazo coupling reaction [9,10], extraction of the azo dye into suitable organic solvent provides a much lower detection limit and improved sensitivity [11]. Neutral Red has been used as cationic dye for spectrophotometric determination of anions like thiocyanate, perchlorate, iodide by solvent extraction [12]. Bleaching of Neutral Red colour with nitrite is slow and it has been monitored at intervals of 5 minutes for the kinetic spectrophotometric determination [13]. But in the presence of bromide ions the reaction of nitrite with Neutral Red goes to completion almost instantaneously and the unreacted dye colour is stable for 2 days.

In the proposed method a known excess of Neutral Red is treated with nitrite in the presence of bromide and acid. The formed diazonium salt is deaminated by the addition of sodium hypophosphite. The method is made more sensitive by extracting the unreacted dye in to organic solvent. The method can be used for the determination of nitrogen dioxide in air, nitrite in water and soil samples and nitrate after reducing the nitrate to nitrite by using copperized cadmium column [14]. The reliability of the method is established by parallel determinations involving diazo coupling reaction [15] and by recovery studies of added nitrite and nitrate.

Experimental

Apparatus

Absorbance values were measured using Carl Zeiss PMQ II Spectrophotometer with 1 cm glass cells (Carl Zeiss, Wurttemberg, Germany). 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. LI-120 digital pH meter (Elico, India) was used for pH measurements.

Reagents

All chemicals used were of analytical reagent grade and distilled water was used for preparing reagent solutions.

1. **Alkaline sodium arsenite absorber solution:** prepared by dissolving 4 g of sodium hydroxide and 1 g of sodium arsenite in 1 L of water.
2. **Triethanolamine (TEA) absorber solution:** prepared by dissolving 15 g of triethanolamine in 1 L of water.
3. **Standard nitrite solution:** prepared by dissolving 0.15 g of dried sodium nitrite (105 °C for 1 h) in 100 mL of water. The nitrite content of the solution is 1000 µg mL⁻¹. Dilute suitable volumes of this solution using sodium arsenite or TEA solution to get 0.4 and 4.0 µg mL⁻¹ of nitrite.

4. **Neutral Red. Basic Red 5 C.I. 50040, Fluka (0.01%):** Prepared by dissolving 0.1 g of neutral red in 1 L of water containing 2.5 mL of 4.25 M sulphuric acid. The dye solution was stable for 30 days. 0.001% dye solution was prepared by diluting 10 mL of 0.01% dye to 100 mL with water and it was stable for 2 days.
5. **Methanolic sulphuric acid:** Prepared by adding 2.5 mL sulphuric acid (Sp.gr. 1.84) to 35 mL water, cooled and diluted to 100 mL with methanol.
6. **NH₃-NH₄Cl Buffer solution (pH 8.5):** Prepared by dissolving 0.53 g of ammonium chloride in 80 mL of water, adjusting pH to 8.5 with 1:1 ammonia (vol/vol) and diluting to 100 mL with water.
7. **Sodium hydroxide (4 M):** Prepared by dissolving 16 g of sodium hydroxide in 100 mL of water.
8. **Formaldehyde (0.5%):** Prepared by diluting 1.3 mL of formaldehyde (38%) to 100 mL with water.
9. **Sodium carbonate (0.5%):** Prepared by dissolving 0.5 g of sodium carbonate in 100 mL water.
10. **Sodium hypophosphite (1%):** Prepared by dissolving 1 g of sodium hypophosphite in 100 mL water.
11. **Solvent for extraction:** Iso- amyl alcohol.

Copperized cadmium column

Metallic cadmium fillings between 40 to 60 mesh were taken, stirred for 2 min with distilled water, stirred for 2 min with 100 mL of 2% copper sulphate solution, and then the supernatant liquid was removed. Metallic cadmium was washed with distilled water till the washings were free from precipitated copper. A glass column (5 mm internal diameter) was carefully filled with prepared material up to 10 cm height on a glass wool support without any air bubbles. The column was washed with 1 M hydrochloric acid after every four runs of nitrate reduction and reused.

Preparation of calibration graph

Aqueous procedure

10 mL aliquots of standard nitrite solution containing 0 – 20 µg nitrite were added to series of 25 mL standard flasks containing 2 mL of 0.01% Neutral Red, 1 mL of 4.25 M sulphuric acid and 1 mL of 1% potassium bromide. This was followed by addition of 1 mL of 1% sodium hypophosphite and mixed. The mixed solution was then diluted to the mark and absorbance was measured at 530 nm against distilled water. Calibration graph obtained was linear but with a negative slope.

Extraction procedure

10 mL aliquots of standard nitrite solution containing 0 – 1.6 µg of nitrite were added to series of 25 mL standard flasks containing 2 mL of 0.001% Neutral Red, 1 mL of 4.25 M sulphuric acid and 1 mL of 1% potassium bromide.

This was followed by addition of 1 mL of 1% sodium hypophosphite and mixed well. The mixed solution was made alkaline by the addition of 2.5 mL of 4 M sodium hydroxide and diluted to the mark. The solution was then transferred into 60 mL separating funnel and extracted with 3 mL of iso-amyl alcohol. The extract was diluted to 5 mL with methanolic sulphuric acid and absorbance was measured at 540 nm against the solvent.

Determination of nitrite and nitrate in water samples

10 mL of the sample was treated with 1 mL of 1 M sodium hydroxide, and centrifuged. Centrifugate was collected, residue was washed with 5 mL portions of water and centrifuged again. All the centrifugates were mixed well and made up to 25 mL.

Nitrite determination: 10 mL of the made up solution was taken and analyzed for nitrite adopting the procedure followed for the construction of calibration graph.

Nitrate determination: 10 mL of the made up solution was taken, treated with 5 mL $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (pH 8.5) and passed through copperized cadmium reductor column at the rate of 1 mL min^{-1} . The column was washed with three 2 mL portions of water, the eluents were collected in a 25 mL standard flask and diluted to the mark. 10 mL of the made up solution was taken and analyzed for total nitrite content.

Determination of nitrite and nitrate in soil samples

A known weight (0.5 g) of soil sample was taken in a 25 mL beaker and extracted with three 5 mL portions of 0.5% sodium carbonate solution. The extracts were filtered through Whatman 41 filter paper. The filtrates were collected and diluted to 25 mL.

Nitrite determination: 10 mL of the made up solution was taken and analyzed for nitrite following the procedure described under preparation of calibration graph.

Nitrate determination: 10 mL of the made up solution was taken and 5 mL of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer was added and mixed. The solution was passed through the reductor column. Total nitrite content was determined following the procedure described under the analysis of water sample.

Determination of nitrogen dioxide in air

Air was drawn through 10 mL of sodium arsenite or aqueous triethanolamine absorber solution at a flow rate of 0.2 L min^{-1} . These absorber solutions have absorption efficiencies of 82 and 95% respectively and the stoichiometric factor for sodium arsenite is unity where as that for triethanolamine is 0.85 [16]. The sampled solution was made up to 50 mL with respective absorber solution. 10 mL of this solution was analyzed for nitrite content following the procedure described under calibration graph. In cases where the nitrite concentration was low the extraction procedure was followed.

Determination of nitrite/nitrate content in analytical grade chemicals

Weighed (2.5 g) sample of analytical grade chemicals were dissolved in water and diluted to the mark in 25 mL standard flask.

Nitrite determination: 5 mL of the made up solution was analyzed for nitrite following the extraction procedure described under preparation of calibration graph.

Nitrate determination: 10 mL of the made up solution was passed through reductor column after the addition of 5 mL of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (pH 8.6) and analyzed for total nitrite following the procedure described for the analysis of water samples.

Determination of nitrate content in medicated tooth paste

Weighed tooth paste sample (0.06 g) was taken, dissolved in water and the clear solution was diluted to 100 mL. 1 mL of the made up solution was taken and analyzed for nitrate content following the procedure described for the analysis of water sample.

Results and discussion

A known excess of Neutral Red, an azine dye having a primary amino group was treated with nitrite under acidic condition in the presence of bromide to form the diazonium salt. Addition of sodium hypophosphite causes deamination with a decrease in absorbance, which is directly proportional to the nitrite concentration. The addition of bromide ion to enhance the rate of diazotization is well known [17] and this concept has been used to complete the reaction instantaneously.

Experimental conditions were optimized and the optimum dye required was 2 mL of 0.01% Neutral Red for aqueous procedure and 2 mL of 0.001% Neutral Red for extraction procedure. Overall acidity of the reaction can vary from 0.12 – 0.25 M, and the acidity was maintained at 0.18 M, which was achieved by the addition of 1 mL of 4.25 M sulphuric acid. The measured absorbance of unreacted Neutral Red at 530 nm was stable for 2 days in aqueous medium.

Attempt was made to extract the dye into suitable organic solvents. The dye was not extractable under acidic condition in organic solvents. The aqueous solution was made alkaline and then extracted with iso-amyl alcohol. Under alkaline condition, the dye was yellow in colour (λ_{max} 460 nm) and shows lower absorbance value as compared to the absorbance at 540 nm (Fig. 1) obtained after the addition of methanolic sulphuric acid. In acidic condition absorbance maxima was shifted to 540 nm from 530 nm as observed in the case of aqueous solution. Several solvents like CHCl_3 , toluene, iso-butyl methyl ketone (IBMK), iso-amyl acetate, iso-amyl alcohol were tried for extraction. Iso-amyl alcohol showed higher blank value and maximum difference between sample and blank for a given concentration of

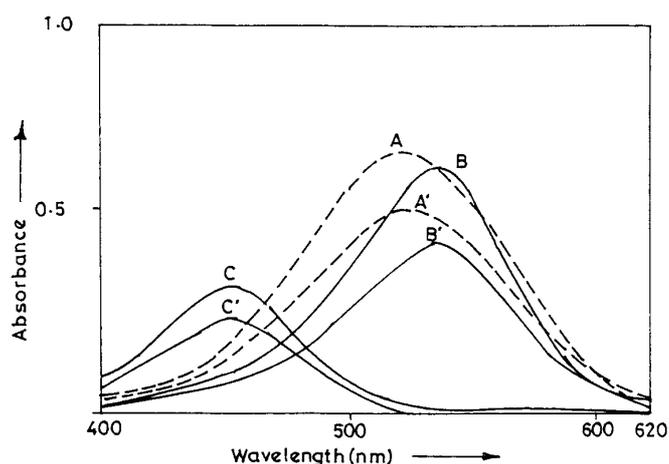


Fig. 1. Absorption spectra. (---) A Reagent blank (2 mL of 0.01% neutral red) against water. A' Same as A with 8 µg NO₂⁻. (—) B Reagent blank (2 mL of 0.001% neutral red) against amyl alcohol under acidic condition. B' Same as B with 0.8 µg NO₂⁻. C Same as B under alkaline condition. C' Same as B' under alkaline condition.

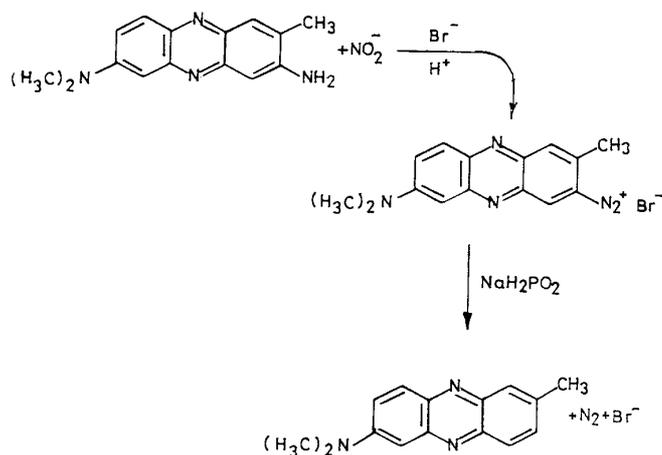


Fig. 2. Species responsible for colour.

nitrite (Tab. I). Two blanks were prepared for this system. The reagent blank which contained optimum concentrations of all reagents except nitrite gave maximum absorbance at 540 nm. The other blank prepared in the absence of nitrite and Neutral Red, exhibited absorbance comparable to that of the solvent. Hence all measurements were made against the solvent.

The calibration graph for aqueous procedure was obtained by plotting absorbance values at 530 nm against nitrite concentration. Beer's law was obeyed over the range 0 – 20 µg of nitrite in an overall aqueous volume of 25 mL. The calibration graph is a straight line, obeying equation $y = -0.020x + 0.673$, where y is the absorbance and x (µg) is the amount of nitrite, with correlation coefficient (r) – 0.997. The precision of method has been established at 8 µg nitrite,

Table I. Extractability of dye into various solvents (NO₂⁻ = 1.2 µg)

Solvent ^a (volume)	λ_{max}	Absorbance	
		Blank	Sample
1. CHCl ₃ (2.5 mL)	535	0.410	0.235
2. CCl ₄ (2.5 mL)	535	0.305	0.175
3. Toluene (2.5 mL)	535	0.390	0.220
4. IBMK (3 mL)	535	0.465	0.250
5. Iso-butanol (5 mL)	540	0.510	0.315
6. Iso-amyl acetate (3 mL)	535	0.410	0.280
7. Iso-amyl alcohol (3 mL)	540	0.570	0.335

^a Based on the solubility of solvent in aqueous phase, different volumes were used. In all cases the extract was diluted to 5 mL with methanolic sulphuric acid.

Table II. Interference studies (NO₂⁻ = 8 µg).

Interferent	Amount tolerated (µg)
Cl ⁻ , CO ₃ ²⁻ , C ₂ O ₄ ²⁻ , SO ₄ ²⁻ , citrate, tartrate, formaldehyde	10 000
PO ₄ ³⁻ , NO ₃ ⁻ , Cr ³⁺ , Co ²⁺ , Fe ²⁺ – Fe ³⁺ , Ca ²⁺ , Al ³⁺ , Mg ²⁺ , Ni ²⁺ , Cu ²⁺ , Cd ²⁺ , Zn ²⁺ , Mn ²⁺	1 000
Hg ²⁺	250
Sulphite	50
^a Sulphite	200
Sulphide	10
^b Sulphide	20
^c Ba ²⁺	1 000

^a Treated with 2 mL of 0.5% HCHO solution prior to nitrite determination.

^b Treated with 1 mL of 1000 ppm Zn²⁺, after adjusting pH to 6, centrifuged and centrifugate is taken for further analysis.

^c Treated with 1 mL of 2% K₂SO₄, centrifuged, centrifugate taken for further analysis.

which gave an relative standard deviation (RSD) of 2.1% ($n = 10$).

In the case of the extraction procedure the Beer's law was obeyed at 540 nm over the range 0 – 1.6 µg nitrite. The calibration graph is a straight line, obeying the equation $y = -0.188x + 0.559$, where y is the absorbance and x (µg) is the amount of nitrite, with correlation coefficient (r) – 0.993. The precision of the method has been established at 1.2 µg nitrite, with RSD as 2.4% ($n = 10$). Enhancement in molar absorptivity was observed in the extraction procedure ($\epsilon = 4.3 \times 10^4$ L mol⁻¹ cm⁻¹) as compared to aqueous procedure ($\epsilon = 2.5 \times 10^4$ L mol⁻¹ cm⁻¹).

Nature of the species responsible for colour

A known excess of Neutral Red on treatment with nitrite solution undergoes diazotization in acidic medium

Table III. Determination of NO₂ in laboratory fume cupboard.

Absorbing solution ^a	Volume of air sampled ^b (L)	Nitrogen dioxide found			
		Neutral Red method		NEDA method	
		NO ₂ ⁻ (μg) in 10 mL	NO ₂ ^c (ppb)	NO ₂ ⁻ (μg) in 10 mL	NO ₂ ^c (ppb)
Sodium arsenite	20	5.00	811	5.00	811
	10	1.75	568	1.74	564
TEA	20	5.25	865	5.27	868
	5 ^d	0.85	560	0.86	566

^a Sampling rate = 0.2 L min⁻¹, collected in 10 mL (diluted to 50 mL).

^b Sampled on different days.

^c Concentration NO₂ (ppb) (in sodium arsenite) = $\frac{NO_2^- (\mu g) \times 5 \times 532}{0.82 \times V}$

$$NO_2 \text{ (ppb) (in TEA)} = \frac{NO_2^- (\mu g) \times 5 \times 532}{0.95 \times 0.85 \times V}$$

V is the volume of air sampled at 25 °C and 101.3 kPa.

^d Extraction procedure was adopted.

Table IV. Determination of nitrate^a in water samples.

Sample	Added nitrate ^b (μg)	Total nitrite ^c found (μg) in 10 mL		Recovery of added nitrate (%)		Nitrate in water sample ^d (mg.L ⁻¹)	
		Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method
Distilled water	10	7.35	7.45	99.1	100.4	–	–
Ground water (Borewell)	–	21.88	22.20	–	–	2.95	2.99
Sea water ^e	10	29.25	29.60	99.3	99.7	2.94	2.99
	–	129.10	131.88	–	–	17.40	17.76
	10	136.41	139.28	98.5	99.7	17.39	17.76

^a Nitrite was not detected.

^b Values correspond to nitrate present in 10 mL of sample.

^c Total nitrite (μg) = nitrite originally present (μg) + nitrite formed by reduction of nitrate (μg), average of 3 values.

^d Nitrate (mg L⁻¹) = $\frac{[\text{Total nitrite } (\mu\text{g}) - \text{nitrite present } (\mu\text{g})]}{10} \times \frac{62}{46}$.

^e Bay of Bengal, Chennai coast, India.

Table V. Determination of nitrate^a in soil samples.

Weight of soil (g)	Added nitrate ^b (μg)	Total nitrite ^c found (μg) in 25 mL extract		Recovery of added nitrate (%)		Nitrate in soil sample ^d (μg g ⁻¹)	
		Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method
0.5	–	65.63	65.75	–	–	176.9	177.5
	5	69.30	69.48	98.9	100.5	176.8	177.3

^a Nitrite was not detected.

^b Values correspond to nitrate present in 25 mL of the extract.

^c Total nitrite (μg) = nitrite present (μg) + nitrite formed by reduction of nitrate (μg), average of 3 values.

^d Nitrate in soil (μg g⁻¹) = $\frac{[\mu\text{g of total nitrite} - \mu\text{g of nitrite present}]}{\text{g of soil}} \times \frac{62}{46}$.

Table VI. Determination of nitrate/nitrite in reagents (analytical grade).

Sample	Added nitrite ^a (μg)	Added nitrate ^b (μg)	Nitrite content ^c (μg)		Total nitrite ^d content (μg)		Recovery of added nitrite (%)		Recovery of added nitrate (%)		Nitrite in sample ($\mu\text{g g}^{-1}$)		Nitrate in Sample ($\mu\text{g g}^{-1}$)	
			Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method
KBr	-	-	-	-	6.75	6.97	-	-	-	-	-	-	9.10	9.39
(s.d. fine India)	-	5.0	-	-	10.40	10.65	-	98.4	99.2	-	-	-	9.02	9.35
K ₂ SO ₄	-	-	-	-	2.25	2.30	-	-	-	-	-	-	3.03	3.10
(BDH India)	-	5.0	-	-	5.95	6.00	-	99.7	99.7	-	-	-	3.02	3.09
(NH ₄) ₂ SO ₄	-	-	-	-	5.75	5.64	-	-	-	-	-	-	7.75	7.60
(Ranbaxy India)	-	5.0	-	-	9.40	9.37	-	98.4	100.5	-	-	-	7.67	7.63
KNO ₃ ^f	-	-	1.14	1.16	-	-	-	-	-	-	2.28	2.32	-	-
(E. Merck India)	0.4	-	1.53	1.56	-	-	97.5	100.0	-	-	2.26	2.32	-	-
NH ₄ NO ₃ ^f	-	-	0.25	0.24	-	-	-	-	-	-	0.50	0.48	-	-
(BDH India)	0.4	-	0.64	0.64	-	-	97.5	100.0	-	-	0.48	0.48	-	-

^a Values correspond to nitrite present in 5 mL of the solution.^b Values correspond to nitrate present in 10 mL of the solution.^c Nitrite content (μg) in 5 mL of solution, average of 3 values.^d Total nitrite (μg) = Nitrite present (μg) + Nitrite formed by reduction of nitrate (μg), average of 3 values.^e Nitrate ($\mu\text{g g}^{-1}$) = [μg of total nitrite/g of sample - μg of nitrite present/g of sample] \times 62/46.^f Extraction procedure was adopted.

Table VII. Determination of nitrate in medicated tooth paste.

Weight of sample ^a (g)	Added nitrate ^b (µg)	Nitrite content ^c (µg) (After reduction)		Recovery of added nitrate (%)		Nitrate in tooth paste ^d (mg g ⁻¹)	
		Neutral Red method	NEDA method	Neutral Red method	NEDA method	Neutral Red method	NEDA method
		0.0593	– 10	12.50 19.95	12.23 19.70	– 100.4	– 100.6

^a Sample as such weighed and diluted to 100 mL.

^b Values correspond to nitrate present in 1 mL of sample solution.

^c Nitrite content (µg) = Nitrite formed by reduction of nitrate, average of 3 values.

^d Nitrate in tooth paste (mg g⁻¹) = µg of nitrite $\times 10^{-3} \times \frac{62}{46} \times 100 \times \frac{1.0}{0.0593}$.

Sample - NITRA, Eros Pharma Ltd., Bangalore - 58, India.

containing potassium bromide. The diazonium salt on treatment with sodium hypophosphite undergoes deamination [18] and causes a decrease in absorbance proportional to the concentration of added nitrite. The absorbance of the unreacted Neutral Red is measured (Fig. 2).

Interference studies

In order to evaluate the suitability of the method for the determination of nitrite in water and soil samples, the interference of several ions in the determination was studied (Tab. II). Tolerance limits of various ions, after adding suitable masking agents were established in presence of 8 µg nitrite. Any ion causing a change in absorbance of the order of ± 0.02 from that obtained in the absence of any interfering species was taken as sign of interference. Effect of common air pollutants like sulphur dioxide, hydrogen sulphide and formaldehyde in determination of nitrogen dioxide was also studied, the species were introduced in the form of their respective anions. Formaldehyde did not interfere up to 10 000 µg, while sulphite at concentrations above 50 µg interfered causing increase in absorbance value. However higher concentrations (up to 200 µg) of sulphite can be tolerated by the system if it is held as bisulphite adduct, which was achieved by addition of 2 mL of 0.5% HCHO solution to the sample prior to nitrite determination. Sulphide is tolerated up to 10 µg, at higher concentrations (up to 20 µg) interference was overcome by precipitating as zinc sulphide, by the addition of 1 mL of 1000 ppm zinc(II) ion to the sample solution and adjusting the pH to 6. The solution was centrifuged and clear supernatant liquid was taken for nitrite determination.

Applications

The proposed method has been applied for the determination of residual concentration of nitrogen dioxide in laboratory fume cupboard, where brass samples were treated with nitric acid for the determination of copper content (Tab. III). In order to evaluate the method, parallel determinations were

carried out making use of the diazo coupling reaction [15] between para-nitroaniline and *N*-(1-Naphthyl) ethylene diamine dihydrochloride (NEDA).

The proposed method was also effectively used for the determination of nitrate and nitrite in water (Tab. IV), soil (Tab. V) and analytical grade chemicals (Tab. VI). Nitrate content in a medicated tooth paste sample (Tab. VII) was also determined. Results showed that they were comparable with those obtained from determinations involving diazo coupling reaction and recovery of added nitrate and nitrite was found to be satisfactory.

Conclusion

The proposed method for the determination of nitrite, nitrate and nitrogen dioxide is simple, sensitive and precise. The calibration graph is linear over the concentration range 0 – 20 µg in aqueous and 0 – 1.6 µg in extraction method and the correlation coefficient being –0.997 and –0.993 respectively. The application of the proposed method for the determination of nitrite and nitrate levels in variety of samples and NO₂ level in air has demonstrated the utility of the method.

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