

SPECTROMETRIC DETERMINATION OF AMMONIUM-NITROGEN WITH QUINOL IN AQUEOUS MEDIUM

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(Received 7 April 2003; Revision accepted 16 July 2003)

ABSTRACT

Quinol is proposed as a reagent for the spectrometric determination of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) in aqueous medium. Quinol forms a pink complex with ammonium salt in aqueous medium. Hydrogen peroxide is needed for colour accentuation. The quinol/ammonium charge transfer complex has absorption maximum (λ_{max}) at 420nm with molar absorptivity (ϵ) of $1.067 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. Beer's law is obeyed up to $6.0 \mu\text{g NH}_4^+\text{-N/ml}$. The correlation coefficient (r) is 0.9962. The optimum quinol concentration and optimum pH are found to be 0.6% (m/v) and 5.00, respectively. The calculated sensitivity is $0.07 \mu\text{g NH}_4^+\text{-N/ml}$. The extent of ionic interference has also been quantitatively evaluated. The most tolerated ion is NO_3^- ($8.00 \times 10^{-3} \text{ mol l}^{-1}$ maximum) and the least tolerated ion is Fe^{3+} ($1.25 \times 10^{-6} \text{ mol l}^{-1}$ maximum). Recovery of $\text{NH}_4^+\text{-N}$ from spiked water sample shows results in the range of 98.49 to 99.69%. The proposed method has been applied to the determination of $\text{NH}_4^+\text{-N}$ in potable water. Results are in good agreement with those obtained by Nessler's method.

KEYWORDS: ammonium-nitrogen, aqueous solution, spectrometry, quinol.

INTRODUCTION

Several methods are available for the determination of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) in aqueous solutions. In nesslerisation method (Lenore et al, 1989), ammonia in water sample is first distilled at pH 9.5 into boric acid solution. This solution which serves as an absorbent for ammonium-nitrogen is then reacted with nessler reagent (Vogel, 1961). Colour is produced by the nessler-ammonia reaction. The ammonium-nitrogen concentration is determined spectrometrically at 400 to 420nm with 1-cm path length, if concentration is in the range of 0.4 to 5mg $\text{NH}_4^+\text{-N/L}$.

In phenate method (Rossum and Villarruz, 1963; Weatherburn, 1967), an intensely blue compound is formed when ammonia reacts with hypochlorite and phenol in aqueous solution. The reaction is catalysed by a manganous salt. Concentration of ammonium-nitrogen is finally determined spectrometrically at 600 to 660nm, if concentration is in the range of $10 \mu\text{g NH}_4^+\text{-N/L}$ to $500 \mu\text{g NH}_4^+\text{-N/L}$.

In titrimetric method (Meeker and Wagner, 1933; Wagner, 1940), the ammonia in water sample is first distilled at pH of 9.5 into indicating boric acid solution (Wagner, 1940). The concentration of ammonium-nitrogen is determined through titration and back titration using standard H_2SO_4 . Concentration must be greater than 5mg $\text{NH}_4^+\text{-N/L}$.

The ammonia-selective electrode method (Banwart et al, 1972) uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. Dissolved ammonia ($\text{NH}_3(\text{aq})$ and NH_4^+) is converted to $\text{NH}_3(\text{aq})$ by raising pH to above 11 with a strong base. $\text{NH}_3(\text{aq})$ diffuses through the membrane and changes the internal solution pH that is sensed by a pH electrode. The fixed level of chloride in the internal solution is sensed by a chloride ion-selective electrode that serves as the reference electrode. Potentiometric measurements are made with a pH meter having an expanded millivolt scale or with a specific ion meter. Concentration range is 0.03 to 1400mg $\text{NH}_4^+\text{-N/L}$.

Quinol (1,4-benzenediol, , which has not been

previously reported as a reagent, is proposed as a reagent for simple and accurate spectrometric determination of ammonium nitrogen in aqueous solution. The other polyphenols including pyrogallol (1,2,3-trihydroxybenzene) have been used for this purpose and the results would be published elsewhere.

MATERIALS AND METHODS

Apparatus

A Unicam SP500 ultraviolet and visible spectrophotometer with matched 1-cm silica cell was used

for absorbance measurements. Jenway 3020 pH meter was employed for pH measurement.

Reagents

All chemicals were of AnalaR, supplied by BDH. Stock solution of ammonium-nitrogen (0.06M or 848.505 $\mu\text{g/ml}$ in $\text{NH}_4^+\text{-N}$) was prepared by dissolving 1.0g di-ammonium hydrogen orthophosphate, $(\text{NH}_3)_2\text{HPO}_4$, in distilled water and diluted to 250ml.

Calibration solution: 0.0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 μg $\text{NH}_4^+\text{-N/ml}$.

Dilute 0.00, 0.01, 0.03, 0.06, 0.09, 0.12, 0.15, and 0.18ml of stock solution of ammonium-nitrogen in 25-ml calibrated flasks with distilled water.

Quinol solution: 1.0% (m/v) or 0.09M.

Dissolve 1.0g quinol in distilled water and dilute to 100ml.

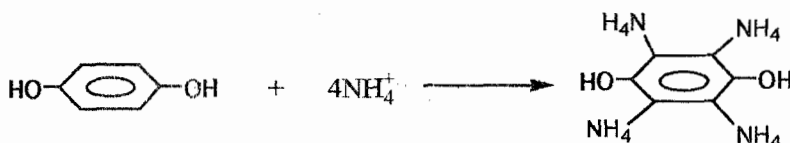
Hydrogen peroxide (H_2O_2) solution: 57.817% (m/v) H_2O_2 .

1M HCl or 1M NaOH solution was used for pH adjustment of the reaction mixture.

Calibration curve

Pipette 0.02ml of the H_2O_2 solution into eight 25-ml calibrated flasks, respectively. Add 0.00, 0.01, 0.03, 0.06, 0.09, 0.12, 0.15, and 0.18ml stock solution of ammonium salt into the flasks, respectively. Finally add 15.00ml of the quinol solution into each flask and make up to mark with distilled water. The first flask contains the reagent blank while the rest are the reaction mixture for calibration curve. Allow them to stand for 35 minutes for maximum colour development. Adjust pH to 5.00 with 1M HCl or 1M NaOH. The absorbance reading was taken for each reaction mixture versus reagent blank at 420nm in matched 1-cm silica cell. The reaction took place at ambient temperature in the range 25-30°C. The graph of absorbance against $\text{NH}_4^+\text{-N}$ concentration was plotted as shown in fig. 6.

The reaction used for quantitative analysis is suggested below:



Preparation of sample solution for analysis

Pipette 5-10ml of sample solution (containing 25-125 μg $\text{NH}_4^+\text{-N}$) into a 25-ml calibrated flask (already containing 0.02ml of the H_2O_2 solution). Add 15.00ml of the quinol solution and make up to mark with distilled water. Procedure for colour development, pH adjustment, ambient temperatures and absorbance readings are as stated under calibration curve. With the absorbance value for the sample solution, read off the corresponding concentration from the calibration curve.

RESULT AND DISCUSSION

Absorption spectra

The absorption spectra of the quinol/ammonium-nitrogen complex (as well as the reagent blank) are shown in fig. 1. The absorbance of the reaction mixture versus reagent blank (A) was far larger than that for reagent blank versus distilled water (B). The wavelength of maximum absorbance, λ_{max} , for the former was located at 420nm.

Effect of quinol concentration

Fig. 2 shows that at pH 5.00 and when $\text{NH}_4^+\text{-N}$ and H_2O_2 concentrations are 5.0 $\mu\text{g/ml}$ and 0.046% (m/v), respectively, and quinol concentration is varied from 0.1 to 0.5% (m/v), the absorbance at 420nm increased from 0.15 [for 0.1% (m/v) quinol] to a constant value of 0.3 [from 0.4-0.8% (m/v) quinol]. Quinol concentration of 0.6% (m/v) [or 15.0ml of 1.0% (m/v) quinol solution in 25-ml calibrated flask] was therefore chosen as the optimum quinol concentration for the method. This is a molar excess of 93.8 fold of quinol over $\text{NH}_4^+\text{-N}$.

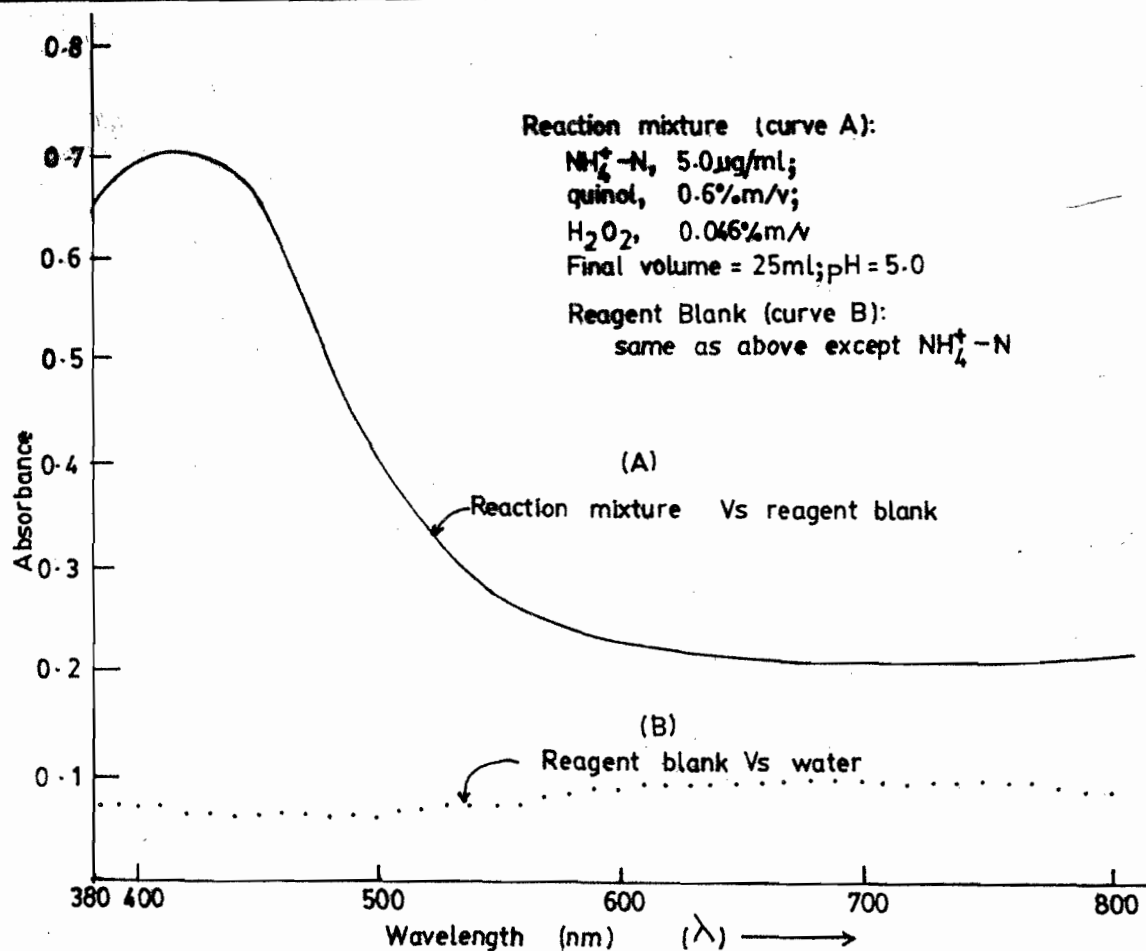
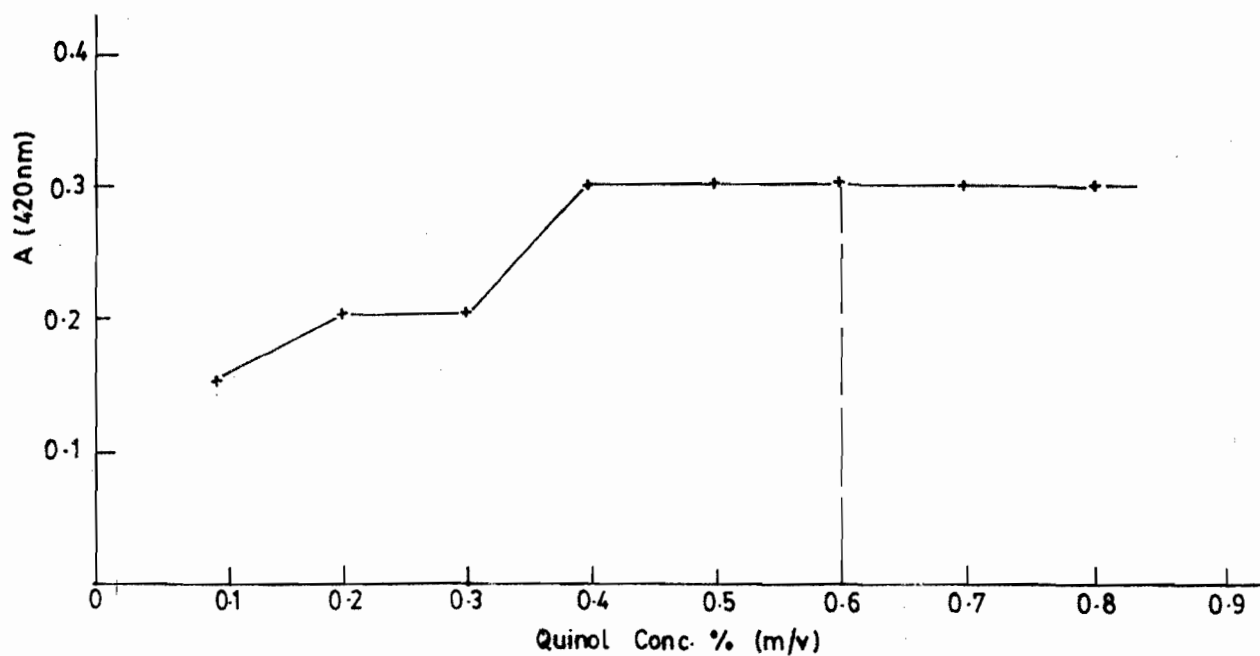
Fig. 1: Absorption spectra for quinol NH_4^+-N complex

Fig. 2: Effect of quinol concentration on absorbance

Effect of pH

When the reaction mixture was composed of 0.046%(m/v) H_2O_2 , $5.0\mu g$ NH_4^+-N/mL and 0.6%(m/v) quinol, and pH varied from 1.00 to 8.00 (using 1M HCl and 1M NaOH solutions), maximum colour intensity (absorbance) was achieved at pH of 5.00. Therefore, all subsequent studies were carried out at pH 5.00 (see fig. 3).

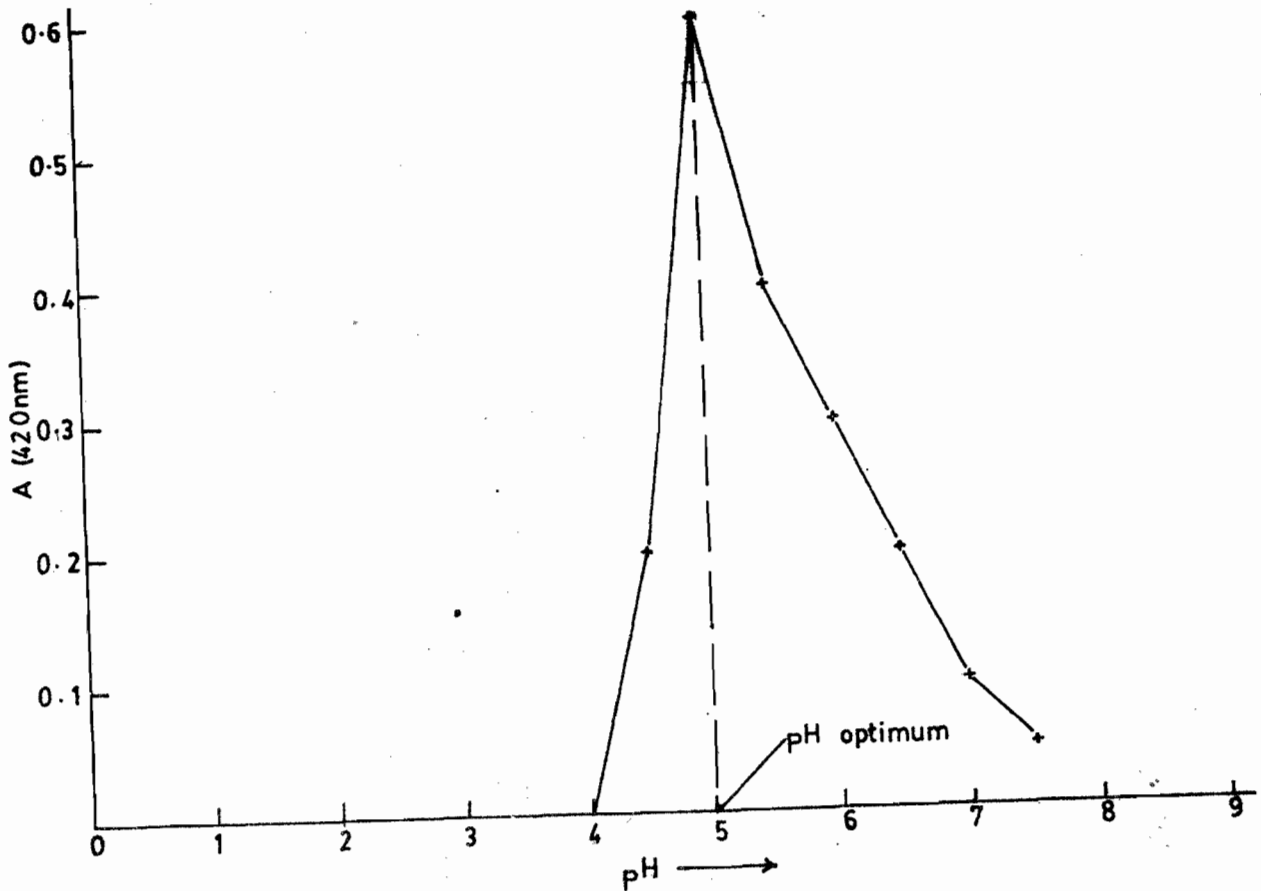


Fig. 3: Effect of pH on absorbance

Effect of hydrogen peroxide

The effect of H_2O_2 on absorbance was investigated when NH_4^+-N and quinol concentrations were $5.0\mu g/ml$ and 0.6%(m/v), respectively. Absorbance readings were taken at 420nm in matched 1-cm silica cell and at pH 5.00. From fig. 4, the reaction mixture showed maximum absorbance at H_2O_2 concentration of 0.046%(m/v). This is equivalent to 0.02ml of 57.81%(m/v) H_2O_2 in 25ml final volume.

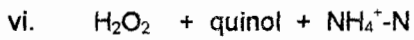
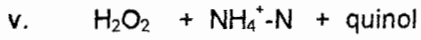
Rate of reaction and the stability of the complex

Fig. 5 shows that, when the concentrations of H_2O_2 , NH_4^+-N and quinol are 0.046%(m/v), $5.0\mu g/ml$ and 0.6%(m/v), respectively, the colour developed after 5 minutes and reached a maximum after 35 minutes. Therefore 35 minutes is chosen as the duration for maximum colour development. The absorbance of the complex remains virtually constant for 3 hours.

Effect of the order of adding reagent

It is possible to have several order of adding reagents as given below:

- i. $NH_4^+-N + \text{quinol} + H_2O_2$
- ii. $NH_4^+-N + H_2O_2 + \text{quinol}$
- iii. $\text{quinol} + NH_4^+-N + H_2O_2$
- iv. $\text{quinol} + H_2O_2 + NH_4^+-N$



From experimental observation it was found that the order mentioned in v provides the best result (maximum absorbance) for the quantitative determination.

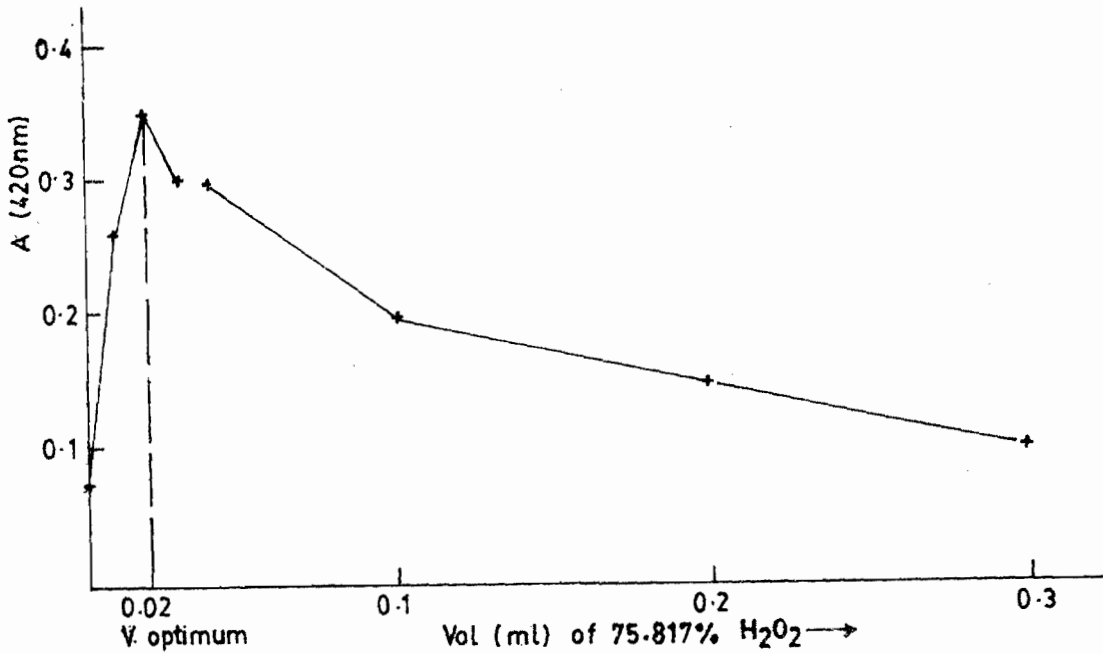


Fig. 4: Effect of H_2O_2 on absorbance

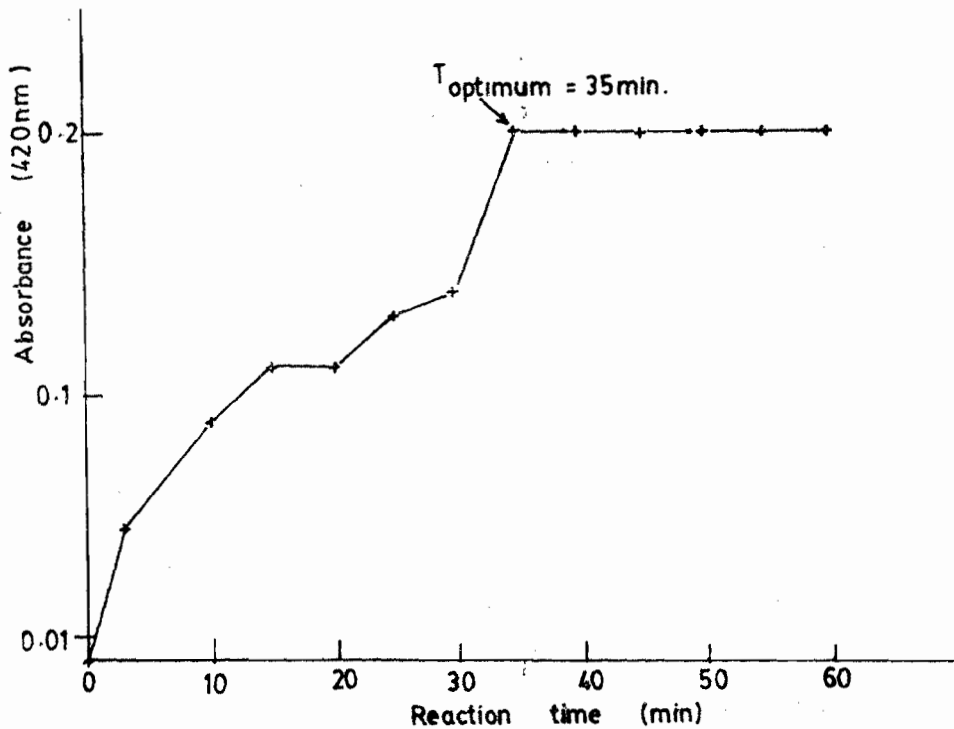


Fig. 5: Effect of reaction time on absorbance

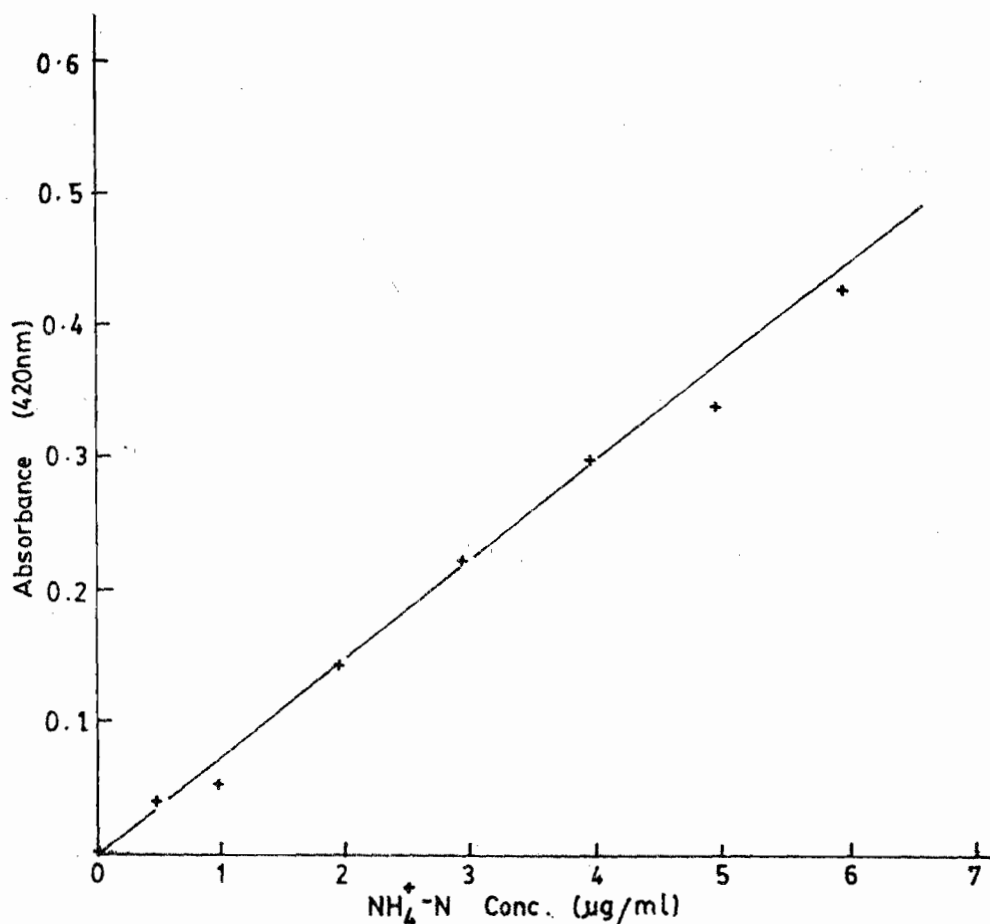


Fig 6: Adherence to Beer's Law

Figures of merit

A series of standard $\text{NH}_4^+\text{-N}$ solutions were prepared. When the quinol and H_2O_2 concentrations were 0.6%(m/v) and 0.046%(m/v), respectively, and total final volume and pH were 25ml and 5.00, respectively, Beer's Law was obeyed up to $6.0\mu\text{g NH}_4^+\text{-N/ml}$ (see fig. 6). The apparent molar absorptivity, (ϵ) (Robert et al, 1974; Donald et al, 1979) of the complex was $1.067 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$. The correlation coefficient, r (Kealey, 1986) was found to be 0.9962 which revealed a high degree of correlation (linearity) between the absorbance and analyte ($\text{NH}_4^+\text{-N}$) concentration. The regression equation (Kealey, 1986) for the curve is given by $y=0.059x + 0.027$, where y is the measured absorbance at 420nm and x the concentration of $\text{NH}_4^+\text{-N}$ in $\mu\text{g/ml}$. The method sensitivity, m.s. (Lenro et al, 1989; A.C.S, 1980; Andres et al 1995; Valentinus et al 1995) was found to be $0.074\mu\text{g NH}_4^+\text{-N/ml}$.

Recovery tests

The accuracy and precision of the proposed method were studied by spiking water samples (de-ionised, well and tap waters) with $\text{NH}_4^+\text{-N}$, and analyzing five replicates of each, using the recommended procedure. Recovery ranged from 98.49% to 99.69%. The standard deviation(s), relative standard deviation (Sr) and confidence limits (95%) for the various spiked samples are given in Table 1

Interference studies

The effect of foreign ions (Saurina and Hernandez, 1995; Susanto et al, 1995; Salinas et al, 1995; Werner and James, 1970) on the absorbance of an $\text{NH}_4^+\text{-N}$ solution ($5.0\mu\text{g/ml}$) is shown in Table 2. Some of the ions chosen, e.g. Na^+ , Ca^{2+} , Mg^{2+} , Cl^- or SO_4^{2-} , are the main components of natural waters, while others, which can form ion-associates, may be present as pollutants, e.g. $\text{As}_{(v)}$, $\text{V}_{(v)}$ or $\text{P}_{(v)}$. The criterion for interference was fixed at $\pm 5.0\%$, thus concentration of foreign ions which cause relative

Table 1: Recovery tests.

	1	2	3	
NH ₄ ⁺ -N {	added (µg/ml):	2.550	7.640	12.73
	originally present (µg/ml):	0.000	0.000	0.00
	found (µg/ml):	2.525	7.525	12.69
% recovery:	99.02	98.49	99.69	
std deviation*, s(µg/ml): ± rel.	0.29	0.16	0.65	
std. deviation, Sr (%):	11.29	2.17	5.09	
95% confidence limit (µg/ml):	2.525±0.360	7.525±0.199	12.69±0.810	

*Repeated 5 times, i.e., average of 5 experimental values for each water sample.

deviations equal to, or lower than, 5.0% were tolerated. Most of the ions tasted were tolerable in a wide range of concentrations. In all cases, the concentrations of the possible interfering species in natural waters are far lower than those found as the maximum tolerated in Table 2.

Table 2: Effect of foreign substances on the absorbance of an NH₄⁺-N of 5.0µg/ml

S/N	Species	Added as	Tolerated concentration (mol l ⁻¹)	*Relative deviation (%)
1	Na ⁺ , ClO ₄ ⁻	NaClO ₄ ·H ₂ O	6.65x10 ⁻³	5.0
2	K ⁺ , NO ₃ ⁻	KNO ₃	8.00x10 ⁻³	-5.0
3	Al ³⁺ , K ⁺ , SO ₄ ²⁻	AlK(SO ₄) ₂ ·12H ₂ O	2.00x10 ⁻⁶	3.8
4	NO ₂ ⁻ , Na ⁺	NaNO ₂	3.00x10 ⁻³	-2.5
5	ASO ₄ ³⁻ , Na ⁺	Na ₂ HASO ₄ ·7H ₂ O	5.13x10 ⁻⁵	3.8
6	WO ₄ ²⁻ , Na ⁺	Na ₂ WO ₄ ·2H ₂ O	3.00x10 ⁻⁶	-4.1
7	PO ₄ ³⁺ , Na ⁺	NaH ₂ PO ₄ ·2H ₂ O	5.13x10 ⁻⁵	1.4
8	CO ₃ ²⁻ , Na ⁺	Na ₂ CO ₃ (anhy)	7.00x10 ⁻⁵	-4.4
9	Cl ⁻ , K ⁺	KCl	7.98x10 ⁻³	-4.4
10	Mg ²⁺ , SO ₄ ²⁻	MgSO ₄ ·7H ₂ O	4.00x10 ⁻³	-4.7
11	Ca ²⁺ , SO ₄ ²⁻	CaSO ₄	6.00x10 ⁻³	4.1
12	Fe ³⁺ , SO ₄ ²⁻	Fe ₂ (SO ₄) ₂	1.25x10 ⁻⁶	5.0
13	V _(v) ⁵⁺	V ₂ O ₅	1.32x10 ⁻⁵	-4.5

$$\text{*Relative deviation} = \frac{A_{\text{without interference}} - A_{\text{with interference}}}{A_{\text{without interference}}} \times 100\%$$

where A = absorbance

Application

The proposed method was applied to the determination of ammonium-nitrogen (NH₄⁺-N) in some natural and potable water. Results were compared with those obtained by a standard spectrometric method, Nessler's method. As shown in Table 3, both methods are in good agreement.

Table 3: Determination of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) in water samples. Concentrations, $\mu\text{g NH}_4^+\text{-N/ml}$, given are the average of three replicates.

Sample	Proposed method	Standard method
Tap water	ND	ND
River water	2.65	2.71
Well water	ND	ND

ND = not detected

CONCLUSION

The proposed method provides an alternative method for the determination of ammonium-nitrogen ($\text{NH}_4^+\text{-N}$) up to $6.0\mu\text{g/ml}$ in aqueous solution. This study provides more insight into the environmental chemistry involving ammonium-nitrogen. Since ammonium-nitrogen is a very important pollution index, knowledge of its concentration in aqueous system is essential in pollution studies.

The advantages of this analytical method are given below:

- (a) the method is cheap and affordable to laboratories in third world countries.
- (b) Sophisticated equipments are not required. The pH meter and uv-visible spectrometer are needed.
- (c) Hazardous chemical like mercuric chloride is not required.
- (d) It is faster than titrimetric method normally used for this purpose.

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