

Spectrophotometric Determination of Ammonium Ion In Soil and Water by Flow Injection Analysis

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Summary: A flow injection spectrophotometric method based on the nitration of indophenol with ammonium ion and sodium hypochlorite in alkaline media is described. The relative standard deviation over the range of 4-24 ppm is 0.6 - 1.2% (n=6) at a sampling rate of 30 h⁻¹. The method is demonstrated by analyzing ammonium ion in soil and water.

Introduction

Nitrogen is essential in maintaining the balance of life in natural ecosystem. However, undesirable nitrogen in the form of nitrates and ammonium ion as a results of man's activity is not only a pollutant but a potential health hazard [1]. It is clear that there is a need for *in situ* analytical techniques for monitoring soil and water quality due to increased public interest and awareness. This necessitated the development of reliable analytical methodologies that meet specified requirement for accuracy, precision and limit of detection and if possible can be automated for higher sample throughput. There are several reported methods for the determination of ammonium ion, principally by ion-selective electrodes [2-5], spectrophotometry [6,7], chemiluminescence [8] and solid state detectors [9,10]. Conventional spectrophotometric detection is potentially very attractive for field use because a wide range of selective and sensitive reagents are available for various inorganic and organic species [11].

Flow injection analysis (FIA) is a rapid, simple and reproducible technique for the determination of metal and non-metal ions because reaction conditions can be controlled by the optimization of experimental parameters such as flow rate, coil length, diameter of tubing etc.

This paper describes a flow injection procedure for soluble ammonium ion determination in soil and water samples involving indophenol reagent.

Results and Discussion

Optimization of FIA manifold

The manifold is optimized with respect to reagents concentration, flow rate, coil length, sample volume and temperature as shown in Table-1. The effect of phenol concentration were studied over the range (0.05 M - 0.30 M) while all other variables were kept constant. The concentration of ammonium ion was 1×10^{-3} M. The absorbance increased from 0.05 M - 0.15 M and no appreciate increase in absorbance was observed above 0.15 M due to the saturation of other reagents with respect to phenol concentration. Sodium nitroprusside act as a catalyst for the reaction of ammonium ion with phenol. The rate of reaction is therefore dependent on the concentration. The effect of sodium nitroprusside was investigated over the range (0.01 - 0.15%). The concentration of sodium nitroprusside (0.1%) was the rate limiting concentration for ammonium (1.0×10^{-1} M) over the range studied. The effect of sodium hypochlorite (1.0 - 5.0%) and sodium hydroxide (0.05 - 0.25 M) were studied for maximum absorbance separately. Sodium hypochlorite (2%) and sodium hydroxide (0.15 M) were the rate limiting concentration.

The effect of mixing coil length on the sensitivity was also investigated over the range of 5-250 cm (0.5 mm i.d.). Increasing the coil length from 50-200 cm increased the absorbance due to the increased residence time in the manifold. However, at larger coil length (250 cm), the absorbance decreased due to the increase in dispersion. The mixing coil length of 200 cm was used for

Table-1: Effect of variables on indophenol formation

Phenol (M)	0.05	0.10	0.15	0.20	0.25
Absorbance*	0.042	0.065	0.069	0.630	0.600
Nitroprusside (%)	0.01	0.05	0.10	0.15	0.20
Absorbance*	0.072	0.086	0.062	0.047	0.044
Sodium Hydroxide (M)	0.05	0.10	0.15	0.20	0.25
Absorbance*	0.011	0.114	0.105	0.093	0.058
Sodium Hypochlorite (%)	1.0	2.0	3.0	4.0	5.0
Absorbance*	0.053	0.124	0.157	0.142	0.130
Flow rate (ml min ⁻¹)	0.2	0.4	0.6	0.8	1.0
Absorbance*	0.062	0.120	0.135	0.100	0.090
Coil length (cm)	50	100	150	200	250
Absorbance*	0.073	0.12	0.150	0.170	0.150
Temperature (°C)	20	30	40	50	60
Absorbance*	0.010	0.060	0.130	0.120	0.100

*Mean of 3 injection

subsequent investigation. The effect of flow rate was studied over the range of 0.16-0.9 ml min⁻¹. The absorbance increased from 0.16 - 0.6 ml min⁻¹ and further increase in flow rate decreased the sensitivity due to the increased dispersion of sample zone at longer residence time.

The rate of indophenol formation is largely dependent on the temperature, therefore the mixing coil was thermostated for maximum sensitivity. The effect of temperature was studied over the range of 20-70°C. The rate of reaction was maximum at 40°C. The effect of time was studied by carrying out the reaction at different time and the ammonium ion concentration was 18 ppm. It was found that 15 minutes were sufficient for full colour development and the colour remained stable for 12 hrs at 40°C.

Calibration graph for ammonium ion

A series of ammonium ion standard solution were injected into the optimized system. A linear calibration graph was obtained between absorbance and ammonium ion concentration over the range 4-24 ppm. The limit of detection (2 x blank signal) was 0.1 ppm. The sampling rate was 30 h⁻¹, the relative standard deviation (r.s.d.) was 0.6-1.2% (n=6) over the range investigated.

Analysis of soil and water samples

The FIA-spectrophotometric method has a great potential for the analysis of real samples. This was confirmed by the results obtained for ammonium ion in soil and water samples as shown in Table-2. The results were in good agreement with the

Table-2: Determination of ammonium ion in soil and water samples.

Soil sample	Proposed method* (ppm)	Reference method** (ppm)
1.	8.6 ± 0.4	8.4 ± 0.1
2.	16.4 ± 0.6	16.2 ± 0.3
3.	6.8 ± 0.3	6.2 ± 0.4
4.	12.4 ± 0.6	11.9 ± 0.3
Water samples		
1.	7.5 ± 0.4	7.2 ± 0.2
2.	5.9 ± 0.5	5.6 ± 0.4
3.	4.6 ± 0.3	4.1 ± 0.1
4.	6.4 ± 0.2	6.0 ± 0.3

* Mean of 3 injections.

** [Ref. No. 11]

reference spectrophotometric method. This indicates the validity of the method for ammonium ion determination.

Interferences

Table-3 shows the effect of various cations and their concentration on the absorbance compared with ammonium ion (1x10⁻³M). The only significant interferences were from cadmium(II), cobalt(II) and copper(II), which had positive effect on absorbance. In real samples cadmium, cobalt and copper have to be present in 10 fold and 100 fold excess. In real samples these metals could be removed by the addition of masking agents.

Table-3: Effect of diverse ions (1x10⁻³M) on the determination of ammonium ion (1x10⁻³M).

Diverse ions	Absorbance*
Ammonium	0.23
Calcium	0.01
Magnesium	0.00
Copper(II)	0.02
Phosphate	0.04
Cobalt(II)	0.02
Cadmium(II)	0.03
Zinc (II)	0.01
Nitrate	0.01
Urea	0.01

*Mean of 3 injections.

Experimental

Reagents and solutions

Phenol stock solution (0.3 M) was prepared by dissolving 5.48 g of phenol in 200 ml of water. Sodium nitroprusside stock solution (0.2%) was prepared by dissolving 0.2 g of sodium nitroprusside in 100 ml of water, stored in brown bottle in a refrigerator and used whenever required. Sodium

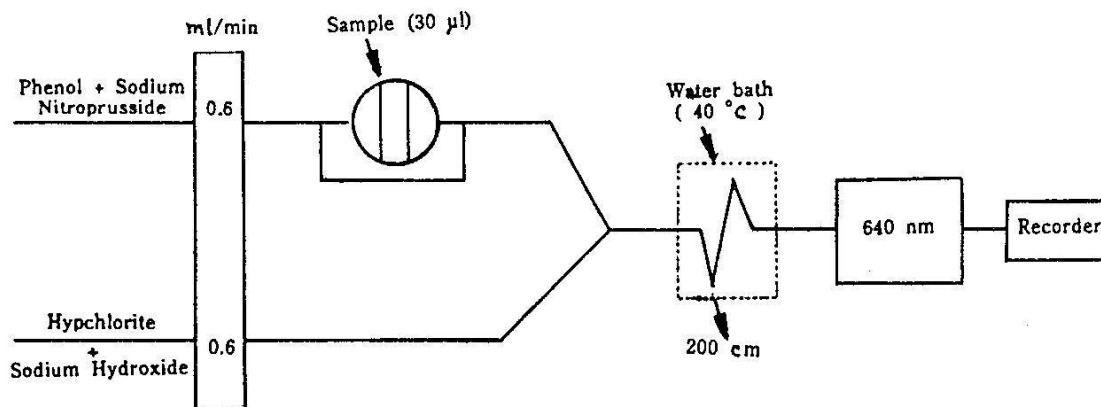


Fig. 1: FIA Manifold for the determination of ammonium ion.

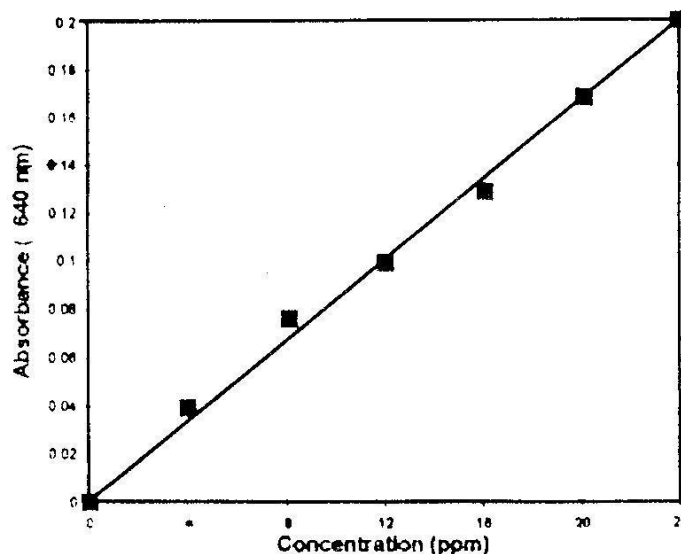


Fig. 2: Calibration graph for ammonium ion determination.

hypochlorite solution (3% v/v) was prepared and content of hypochlorite was checked iodometrically. Sodium hydroxide solution (0.3 M) was prepared by dissolving 2.4 g of sodium hydroxide (oven dried at 120°C for 1 hr) in 200 ml of water. Ammonium chloride stock solution (1000 ppm) was prepared by dissolving 0.446 g of ammonium chloride in 100 ml of water. Working standards were prepared by serial dilution of the stock solutions. All reagents were of analytical grade (Merck, BDH) and distilled-deionized water was used throughout.

Sample preparation

The soil samples, originating from Balochistan Agricultural Research Institute, Quetta were extracted [12] by weighing accurately 20 g of air-dried soil sample (crushed to pass through a 40-mesh sieve) into a beaker, pasted with deionized water and left for 3 hrs. The dissolved material was extracted using suction pump and also centrifuged at 5000 rpm and then analyzed by using flow injection procedure.

Fresh water samples were collected from various locations of Quetta city and analyzed after collection without further treatment.

Instrumentation and procedure

Figure 1 shows a flow injection manifold for the determination of ammonium ion. Ammonium standards (30 μ l) were injected into the stream of phenol (0.15 M) containing sodium nitroprusside (0.05%) using a rotary injection valve (Reodyne 5020). The sample along with reagents were mixed down stream at a T-piece with another stream containing sodium hypochlorite (3.0%) and sodium hydroxide (0.1 M). The sample and the reagents were allowed to mix in a dispersion coil (200 cm long and 0.5 mm i.d.). The mixing coil was immersed in water bath at 40°C. As the dispersion zone reached the flow cell, the absorbance was monitored at 640 nm by using a spectrophotometer (Hitachi, U1100, Japan). The detector output was fed to a strip chart recorder (Kipp and Zonen BD 40). The manifold tubing were teflon (0.5 mm i.d.) and the reagents were pumped at the same flow rate (0.6 ml min⁻¹) per channel by using a peristaltic pump (Ismatec Reglo 100).

Conclusion

The FIA-spectrophotometric method provides a simple, rapid and inexpensive mean of determining metal ions in trace levels. Methods for eliminating

interfering elements would allow a highly selective and sensitive determination of ammonium ion in real samples.

References

1. E.H. Hansen, A.K. Ghose and J. Ruzicka, *Analyst*, **102**, 705 (1977).
2. J. Slanina, F. Bakker, J.J. Mols, J.E. Ordeman and A.G.M. Bruyn-Hes, *Anal. Chim. Acta*, **112**, 45 (1979).
3. H. Hara, A. Motoika and S. Okazaki, *Anal. Chem.*, **59**, 1995 (1987).
4. H. Hara, A. Motoika and S. Okazaki, *Anal. Chem.*, **113**, 113 (1988).
5. P.J. Worsfold, *J. Automatic Chemistry*, **16**, 153 (1994).
6. J. Slanina, F. Bakker, A. Bruyn-Hes and J.J. Mols, *Anal. Chim. Acta.*, **113**, 331 (1980).
7. F.J. Krug, J. Ruzicka and E.H. Hansen, *Analyst*, **104**, 47 (1979).
8. T. Murachi and M. Tabata, *Biotechnol. Appl. Biochem.*, **9**, 303 (1987).
9. J.R. Clinch, P.J. Worsfold and F.W. Sweeting, *Anal. Chim. Acta*, **214**, 401 (1988).
10. J.R. Clinch, P.J. Worsfold, H. Gasey and S.M. Smith, *Anal. Proc.*, **25**, 71 (1988).
11. C.P. Xing, L.P. Guo and Z.Q. Ying, *Analyst*, **112**, 909 (1987).
12. M.L. Jackson, *Soil Chemical Analysis*, Printice Hall, New Jersey, USA (1958).