

Determination of Ammonia-N in Environmental Water by Air-segmented FIA

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Abstract: A method for determination of ammonia-N in environmental water by air-segmented flow injection analysis using the colour reaction of phenol and sodium hypochlorite with ammonia was described in this paper. When the reaction temperature is 70 °C and the reaction residence time is 5 minutes, a sample frequency of 60 ~ 90 h⁻¹ can be achieved. The detection limit and relative deviation are 0.05 mg·ml⁻¹ and 4%, respectively. The recovery of this method is 96 ~ 110%, and the determination results of the method are greatly agreement with standard colorimetric method.

Keywords: Air-Segmented FIA, Ammonia-N, Environmental Water, Spectrophotometry

1. Introduction

Organic compounds containing nitrogen (N) can be transferred, by microorganisms, to amine or ammonia which can be transferred successively to nitrite and nitrate salts whose amounts can be represented by ammonia-N. Therefore, the amounts of ammonia-N is an important criterion for environmental water. Generally, ammonia-N was determined by methods such as Nesslerization, colorimetric analysis of phenol and sodium hypochlorite[1,2] and selective ion electrode[3] etc..

Flow injection analysis, because of its merits such as quickness and convenient etc. has been widely used in analytical field since it was

developed from 1975's., meanwhile, the sensitivity of classical analytical method can be enhanced, the analytical time can be shortened, and the procedure of analysis can also be simplified if the classical method is combined with the normal FIA technique. However, the normal FIA technique, because of stratified fluid of carrier which can result in convection dispersion and molecular dispersion in carrier, has two drawbacks: (1). The dispersion of sample zone along axial direction makes the normal FIA technique unsuitable for slow reaction system. (2). It is impossible to solve the heating problems in normal FIA in that heating procedure would cause bubbles (i.e. solved gas and vapouring bubbles) which heavily affect the reproducibility of analytical results

and interfere the spectrophotometry analysis with deflecting on ray. The normal FIA also, on the other hand, have the disadvantages such as limited instrument conditions and long reaction time, etc. Therefore, the method for determination of ammonia-N by using the normal flow injection analysis combined with Nesslerization or phenol and sodium hypochlorite colour development reaction system, because of those disadvantages mentioned above, has a poor detection limit: 0.5 mg.L^{-1} [4] or 5 mg.L^{-1} [5] respectively.

To surmount the disadvantages mentioned above in the normal FIA, a new method, air-segmented flow injection analysis, was reported by Tian et al.[6,7] A special valve was designed to inject the samples and bubbles into the carrier stream in a quantitative manner. Because the sample is accurately sandwiched between two bubbles. Owing to the amount of the air introduced is minimized, the dispersion is limited and the flow rate is stabilized. Hence, reaction temperature can be higher than that of normal FIA.

In this work, the above method was combined with phenol-sodium hypochlorite colorimetric system for determination of ammonia-N in environmental water. When the reaction temperature is $70 \text{ }^\circ\text{C}$, the residence time is 5 minutes and the sample frequency is $60 \sim 90 \text{ h}^{-1}$, the detection limit, relative error and the recovery of this method are 0.05 mg.L^{-1} , 4% and 96-110%, respectively. The results is greatly agreement with the standard colorimetric method.

2. Experimental

Reagents: All chemicals were of analytical reagent grade (Shanghai First Reagent Factory)

Ammonium standard solutions: A stock standard solution was prepared by dissolving 3.8190 g ammonium chloride in ammonia free water and transferred into a 1000 mL volumetric flask and diluted to the mark. This solution contained 1.0 mg.mL^{-1} ammonia-N ($\text{NH}_4\text{-N}$). Working standard solutions of various concentrations were prepared by dilution of the stock standard solution with distilled water.

Solution A: 4.8 g sodium hydroxide was dissolved in 1000 mL distilled water.

Solution B: Phenol 5 g and sodium nitroferricyanide 25 mg were dissolved in water and the solution was diluted to 500 mL with distilled water, then the resulted solution was stored in refrigerator in dark bottle.

Solution C: The solution C was prepared by dissolving 2.5 g sodium hydroxide, 18.7 g disodium hydrogen phosphate and 15.9 g sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$) in water, then sodium hypochlorite in which the effective chlorine is 250 mg (i.e. 5.2%) was added and the solution was diluted to 500 mL by ammonia free distilled water. Finally, the solution was stored in refrigerator in dark bottle.

EDTA solution of 1% (w/v): The solution was prepared by dissolving EDTA 1.0 g in 100 mL distilled water and the solution was adjusted to $\text{pH}=10$ by NaOH solution.

3. Apparatus and Procedure

3.1. A schematic diagram of the apparatus is shown in Fig.1. The sample is aspirated through the sample loop and air is aspirated through tubes in the valve by pump P_1 . The carrier stream flows through a by-pass tube into the reaction tube. When the valve is turned from the sampling to the injection position, an air-segmented sample plug is formed and, after mixing with reagent streams R_1 and R_2 , it enters into the reaction tube. After reaction, the air-segmented sample passes through a debubble chamber where the bubbles are removed, then the sample flows through a flow cell at a speed controlled by pump P_2 , and the absorbency is measured at 625 nm.

3.2. Conditions for experiment: Reaction temperature (t) is $70 \text{ }^\circ\text{C}$ and residence time is 5 minutes. The length of reaction tubing (RC) with 1mm inner radius is 8 M. Carrier (C) is ammonia free water and its flow rate (F_c) is 1.8 mL.min^{-1} . R_1 and R_2 are solution B and solution C, respectively, and both of their flow rate (F_{R1} , F_{R2}) are 0.45 mL.min^{-1} . The volume of flow cell is 130 μl . The rear pump flow rate (F_b) is 0.55 mL.min^{-1} . The aspirating time of sample is 40 sec. and the injection

time is 20 sec.. The paper running rate of recorder is $2 \text{ mm} \cdot \text{min}^{-1}$ and measuring range is 1 mv.

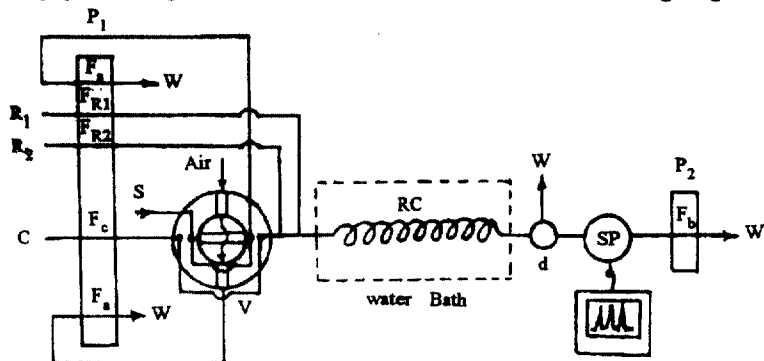


Fig.1. Schematic diagram of the apparatus. P_1, P_2 : peristaltic pumps; S: sample; C: carrier solution; R_1, R_2 : reagents; V: valve; RC: reaction tubing; d: debubbler chamber; SP: spectrophotometer; W: waste.

The apparatus is constructed from a FIA-T1 flow injection analyzer (Instrumental Factory of North-East Electric Power Institute), Model 756 UV-visible spectrophotometer (Yixing Analytical Instrument Factory, Jiangsu), XWT 104 recorder (Dahua Instrumental Factory, Shanghai), a Gilson Minipuls 2 peristaltic pump and PTFE tubing.

4. Results and Discussion

4.1 Influence of phenol concentration (solution B):

Effect of phenol concentration (solution B) on the reaction system is shown in Fig.2. It can be seen, from the Fig.2, that the curve will reach the peak at the

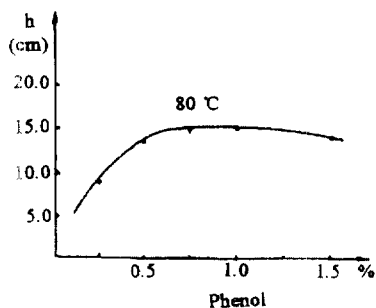


Fig.2. Effect of phenol concentration: $\text{pH}=11.7$, $[\text{NaClO}_3]=0.5 \text{ mg} \cdot \text{mL}^{-1}$, $[\text{phenol}]=1\%$, $[\text{NaClO}_3]=0.5 \text{ mg} \cdot \text{mL}^{-1}$

concentration of phenol 1%, and beyond this point, the curve will draw down from the peak.

4.2. *Effects of sodium nitroferricyanide concentrations:* Both sodium nitroferricyanide and Me_2CO can be used as a catalyst for this method, but the previous is the better one. From Fig.3, it can be seen that this reaction system is related to temperature and residence time, but the concentration of sodium nitroferricyanide do not greatly affect on this method. However, this colour development reaction can hardly process if the catalyst is not added the system.

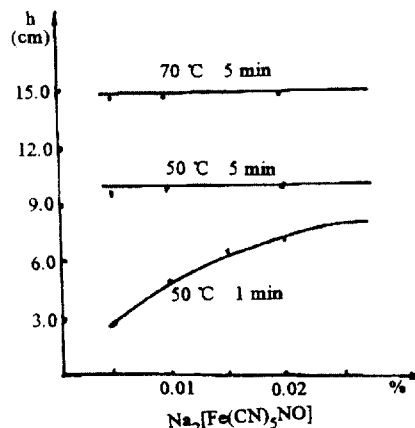


Fig.3. Effect of sodium nitroferricyanide concentration. $[\text{phenol}]=1\%$, $[\text{NaClO}_3]=0.5 \text{ mg} \cdot \text{mL}^{-1}$

4.3. *Effect of the concentration of sodium hypochlorite (effective)*: Fig.4 shows that the peak height of determined signal increased with increase in concentration of sodium hypochlorite, and 0.5 mg.mL⁻¹ sodium hypochlorite concentration is the most suitable for this system. over or lower this concentration, the peak height of determined signal will descend.

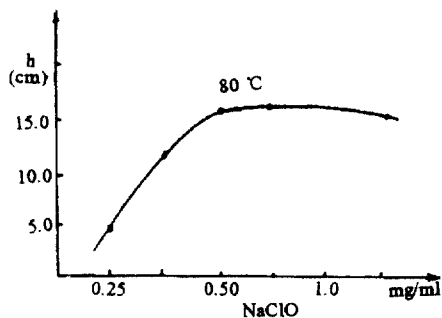


Fig. 4. Effect of sodium hypochlorite concentrations.
[phenol]=1%

4.4. *Effect of reaction temperature and time*: The influences of reaction temperature and reaction time are shown in Fig.5 and Fig.6. From the two Fig., it can be seen that the peak height increased with increase in both reaction temperature and reaction residence time and the peak height will not, however, increase markedly when the reaction temperature is more than 60 °C and the residence time is longer than 5 minutes, from which it can be known that this reaction system is not a kinetics or catalyst kinetics system and the reaction can reach equilibrium state under certain conditions (i.e. the colour of reaction

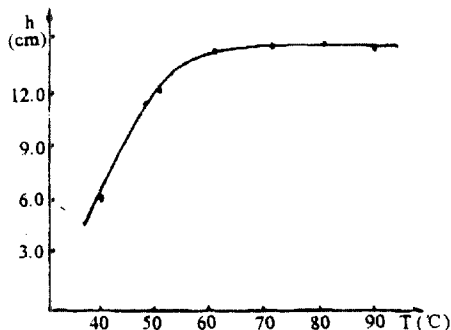


Fig. 5. Effect of reaction temperature.

mixed solution will not change with time and the system state can be sustained stably). To increase the reaction rate, 70 °C temperature and 5 minutes residence time were selected in this paper.

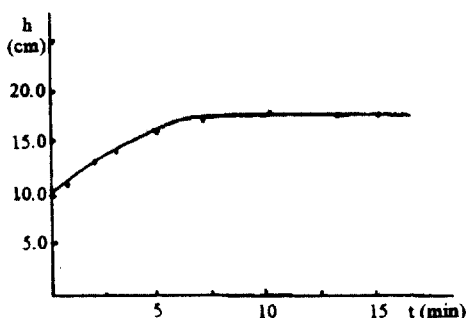


Fig. 6. Effect of residence time

5. The determination of ammonia-N in water

5.1. *Calibration*: Following the above analytical procedure, concentrations of ammonia-N represented in peak height in a series of standard solution of ammonia-N (i.e. ammonium chloride), 0.1 to 0.5 mg.L⁻¹ mixed with EDTA (0.01%) were determined by the air-segmented FIA analysis mentioned above. The calibration curve is obtained in Fig.8 which shows a straight line. The correlation coefficients were 0.999.

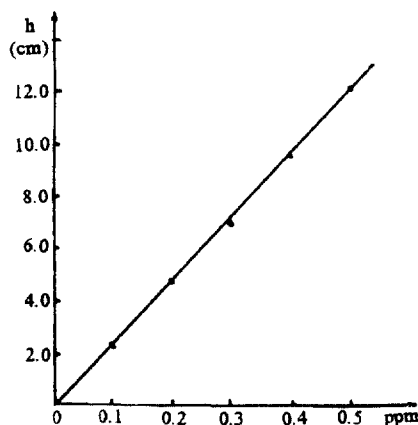


Fig. 8. Calibration curve

5.2. Sample analysis for environmental water: To determine the ammonia-N in environmental water, firstly, the pH data of sample water should be adjusted to about 7, then the sample water must be decoloured and finally filtered by a film of 0.45 μ m. After those above procedures, the handled water was determined by method as in the calibration procedure. The typical response for ammonia-N determination in environmental water in some areas were shown in Fig.7, and the analytical results of ammonia-N in environmental water by this method were compared with that of the standard method in table 1. The table 1 shows that the results determined by this method is greatly agreement with the standard method. The relative deviation of the method is below 4% and the recovery of this system is 96 ~ 110%. Under above conditions, the frequency of sample is 60 ~ 90 h⁻¹.

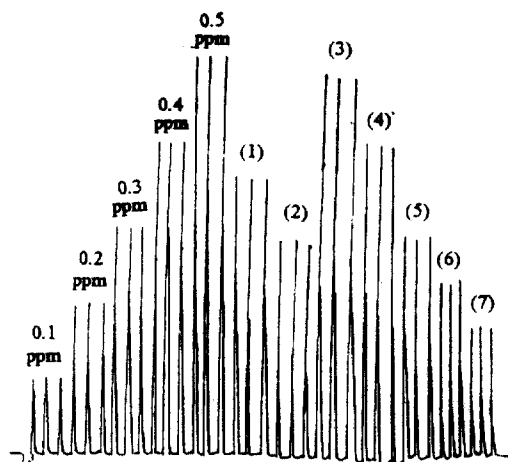


Fig.7. Typical response for ammonia-N determination in environmental water in some areas.

Nanjing: (1). Jimingsi (2). Xuanwuhu. (3). Qinhuaihe
(4) Fuqiao. (5). Mochouhu.

Sichuan Province: (6). 4 Km away from lower of Batang
(7). Dongqu village, Shiqu.

Table 1. The ammonia-N determination results of water samples in varied areas

water name	volume (mL)	peak height	standard method[3] (cm)	proposed method (ppm)	relative error (ppm)	recovery		recovery %
						added (%)	test detnd (ug)	
<u>Nanjing</u>								
Jimingsi	0.50	8.30	6.92	7.06	+2.0	0.20	0.200	100
Xuanwuhu	5.00	6.70	0.582	0.564	-3.1	0.20	0.220	110
Qinhuaihe	0.50	11.55	9.80	9.70	-1.0	0.20	0.196	98
Fuqiao	0.25	9.65	16.16	16.24	+0.5	0.20	0.208	104
Mochouhu	1.00	6.79	2.94	2.86	-2.7	0.20	0.192	96
<u>Sichuan</u>								
4Km away from lower of Batang	5.00	5.76	0.50	0.48	-4.0	0.20	0.198	99
Dongqu village, Shiqu	5.00	3.84	0.50	0.48	-4.0	0.20	0.198	99

6. Conclusion

The ammonia-N can be effectively determined by the air-segmented flow injection analysis which, because of its advantages such as higher reaction

temperature and long residence time, can overcome drawbacks of the normal FIA such as undoing on slow reaction system and heating reaction system. By this method, the ammonia-N can be determined quickly and accurately, and a lower detection limit

was obtained (0.05 mg.L^{-1}). Its large frequency of sample make this method suitable for the determination of ammonia-N when a great number of water samples are in environmental analysis.

7. References

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