Determination of the Total Inorganic and Ammoniacal Nitrogens in Water by Gas-Phase Molecular-Absorption Spectrometry

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Based on a vapor-liquid equilibrium of ammonia, a simplified and rapid technique was developed for the determination of the total inorganic and ammoniacal nitrogens in aqueous solution. Ammonium ion was converted into gaseous ammonia by adding a sodium hydroxide solution to a sample solution. The generated ammonia was directly introduced into a quartz cell in order to measure the molecular absorption. As for the determination of the total inorganic nitrogen, the sample solution was pretreated with titanium(III) chloride solution in order to reduce nitrate and nitrite ions to ammonium ion. The ammonia was then evolved and determined in the same manner as mentioned above. The detection limit (3 S/N) of $0.01 \mu\text{g cm}^{-3}$ for both ammonia and the total inorganic nitrogen was obtained. The calibration graph was linear up to $0.8 \mu\text{gN cm}^{-3}$ for each nitrogen species. The relative standard deviations for five replicate measurements were 3.9, 4.5 and 4.7% for $0.40 \mu\text{g cm}^{-3}$ of nitrogen present in the form of ammonium, nitrate and nitrite ions, respectively. The analytical results for some environmental and industrial water samples are presented.

Keywords Molecular absorption spectrometry, ammonia generation, ammonium, nitrate, nitrite

One of the causes for the proliferation of plankton is known to be the result of an increase in the concentration of tropholytic salts, such as nitrate and phosphate. These salts are supplied by effluents from domestic sewerage, industrial waste water, etc. It is therefore important to determine and regulate the amounts of these species in water. Among inorganic nitrogen compounds existing as ammonium, nitrate and nitrite ions, ammonium ion is commonly determined by the Indophenol Blue method or UV absorption spectrometry; nitrate and nitrite ions are determined by the *N*-(1-naphthyl)ethylenediamine method after both are reduced to nitrite ion by passing through a copper-cadmium column.¹ However, these methods have some problems, such as a lack of sensitivity, troublesome operation and being time consuming.

Van Son *et al.*² and Motomizu *et al.*^{3,4} presented assemblies of a gas-diffusion unit with a microporous PTFE (polytetrafluoroethylene) to determine ammoniacal nitrogen in water. However, the gas-diffusion units used in their methods are not commercially available. On the other hand, an attempt to measure the molecular absorption of ammonia in the gas phase was reported by Creaser.⁵ In his procedure, the gaseous ammonia generated from a strongly basic sample solution was transferred into an absorption cell by a carrier gas to measure the absorbance. However, the moisture and/or mist, which occurred due to the bubbling procedure, were also introduced into the cell to produce a fluctuation of the background absorption. In order to eliminate the

interference, the equipment became intricate.

The vapor-liquid equilibrium method was successfully used for determining mercury in aqueous samples.⁶ In this method, mercury in the gas phase equilibrated with that in the aqueous phase was simply swept and introduced into an absorption cell by a carrier air stream; a bubbling procedure was thus avoided. Based on this principle, a simplified and rapid method was developed for the determination of ammoniacal nitrogen in an aqueous sample solution. Regarding nitrate and nitrite nitrogens, the total amount could also be determined by their prereduction to ammonia with titanium(III) chloride.

Experimental

Apparatus

A molecular absorption of gaseous ammonia was measured using a Shimadzu (Kyoto, Japan) Model AA-650 atomic absorption spectrometer equipped with a Hitachi (Tokyo, Japan) Model QPD-54 strip-chart recorder, a Hamamatsu Photonics (Toyooka, Japan) Model L-555 deuterium discharge lamp and a quartz absorption cell (200 mm $\times$ 8 mm o.d.) of our own making. An apparatus for generating gaseous ammonia comprised a Yamato (Tokyo, Japan) Model M-21 magnetic stirrer, a Taiyo Denki (Osaka, Japan) Model A-1 diaphragm pump, a 120-cm³ reaction vessel and a trap. Each part

Fig. 1 Flow diagram of the gaseous ammonia generation/measurement system. a, Air pump; b, reaction vessel; c, magnetic stirrer; d, D₂ lamp; e, quartz cell; f, trap; g, detector; h, recorder.

of the system was connected to 8-mm i.d. silicone rubber tubing. A schematic diagram of the system is shown in Fig. 1.

Reagents

All of the reagents used were of analytical-reagent grade. An ammoniacal nitrogen standard stock solution ($10.0 \mu\text{gN cm}^{-3}$) was prepared by dissolving 0.660 g ammonium sulfate (Wako Pure Chemical Industries, Osaka, Japan) to 1000 cm^3 with water. A nitrate nitrogen standard stock solution ($15.0 \mu\text{gN cm}^{-3}$) was prepared by dissolving 1.530 g of potassium nitrate (Wako Pure Chemical Industries) to 1000 cm^3 with water. A nitrite nitrogen standard stock solution ($15.0 \mu\text{gN cm}^{-3}$) was prepared by dissolving 0.690 g of potassium nitrite (Wako Pure Chemical Industries) to 1000 cm^3 with water. These standard stock solutions were diluted with water, as required, before use. A sodium hydroxide solution (0.50 g cm^{-3}) was prepared by dissolving sodium hydroxide (Wako Pure Chemical Industries) and diluting with water. A titanium(III) chloride solution (0.25 g cm^{-3} , 2 mol dm^{-3} in HCl) was prepared by dissolving titanium(III) chloride (Wako Pure Chemical Industries) in hydrochloric acid and diluting with water. A tin(II) chloride solution (0.25 g cm^{-3} , 1 mol dm^{-3} in HCl) was prepared by dissolving tin(II) chloride (Wako Pure Chemical Industries) in hydrochloric acid and diluting with water.

Recommended procedure for the determination of total inorganic nitrogen

A 30-cm^3 aliquot of an aqueous sample solution containing not more than $0.80 \mu\text{g cm}^{-3}$ of inorganic nitrogen, 0.50 cm^3 of a titanium(III) chloride solution and 30 cm^3 of a sodium hydroxide solution, and a stirring bar were placed into the reaction vessel. The vessel was then connected immediately with silicone tubes to a quartz cell and a pump (Fig. 1). The mixture in the vessel was stirred for 5 min by means of the magnetic stirrer (1200 rpm). The generated gaseous ammonia

was introduced into the quartz cell with a $2.0 \text{ dm}^3 \text{ min}^{-1}$ carrier gas stream of air. The transient molecular absorption signal at 201 nm was recorded with the spectral band width of 1.0 nm and the peak height was measured. The exhaust gas, which included ammonia vapor, was passed through a trap containing 1.0 M sulfuric acid.

Recommended procedure for determining ammoniacal nitrogen

Ammonium ion initially present in the sample solution was determined by generating gaseous ammonia in the same manner as mentioned above, except in the absence of a reducing agent.

Calculation of the amounts of nitrate and nitrite nitrogens

The amount of nitrogen present in the forms of nitrate and nitrite ions was calculated by subtracting the amount of nitrogen initially present as ammoniacal species from the total amount of nitrogen.

Results and Discussion

Absorption spectrum of gaseous ammonia

Figure 2 shows the molecular absorption spectrum of gaseous ammonia measured using the system mentioned above. The maximum peaks of the absorption spectrum appeared at 197, 201, 205, and 213 nm. The absorption peak at 197 nm, which gives the highest sensitivity among them, was susceptible to absorption due to the water vapor which accompanied the gaseous ammonia and/or due to scattering by dust. Hence, 201 nm, the second highest peak, was selected for the determination of ammonia.

Optimization of the conditions for determining ammoniacal nitrogen

In order to determine the optimum conditions for generating gaseous ammonia, the concentration of sodium hydroxide, the volume ratio of the liquid phase to the gas phase (V_l/V_g), and the mixing time were investigated by recording signals from standard solutions containing $0.40 \mu\text{g}$ of ammoniacal nitrogen. To evaluate the effect of sodium hydroxide on the molecular absorption of ammonia, the added amount of sodium hydroxide to the reaction vessel was varied while keeping the other conditions constant. The analysis was carried out according to the recommended procedure. As Fig. 3 shows, with increasing the concentration of sodium hydroxide in the solution, the generation of gaseous ammonia increased and reached a maximum and constant value in the concentration range of $0.20\text{--}0.35 \text{ g cm}^{-3}$. Thus, 30 cm^3 of a 0.50 g cm^{-3} sodium hydroxide solution was added to adjust the optimum concentration.

The equilibrium of ammonia between the liquid and gas phases depended on V_l/V_g which influenced the sensitivity. The effect of V_l/V_g was thus investigated,

Fig. 2 Molecular absorption spectrum of gaseous ammonia. Scanning speed, 10 nm min^{-1} ; response (time constant), 2 s; ammoniacal nitrogen, $1.0 \mu\text{g cm}^{-3}$.

Fig. 3 Effect of the sodium hydroxide concentration on the generation of gaseous ammonia. Ammoniacal nitrogen, $0.40 \mu\text{g cm}^{-3}$.

where the volume of the reaction vessel and the amount of ammonium ion were kept constant: 120 cm^3 and $0.40 \mu\text{g}$ of ammoniacal nitrogen, respectively. The V_l/V_g value was changed by varying the volume of the liquid phase from 20 to 80 cm^3 , and that of gas phase from 100 to 40 cm^3 . As Fig. 4 shows, the sensitivity was increased by increasing V_l/V_g and then decreased. Since the maximum sensitivity was obtained at a ratio of 1.0, the volume of the liquid phase should be kept at 60 cm^3 and that of the gas phase at 60 cm^3 . Vigorous mixing was not recommended, since an excess amount of moisture and/or mist accompanying the generated bubbles was introduced into the cell, which caused spectral interference. Under a moderate condition at

Fig. 4 Effect of the V_l/V_g ratio on the generation of gaseous ammonia. Ammoniacal nitrogen, $0.40 \mu\text{g cm}^{-3}$.

Table 1 Effect of reducing agents on the reduction of nitrate^a

Reductant	Added ^b	Reduction efficiency, %
Zn powder	0.10 g	20
Al powder	0.10 g	23
Devarda's alloy	0.10 g	42
SnCl_2 solution	$0.25 \text{ g cm}^{-3} \times 0.50 \text{ cm}^3$ (0.13 g) ^c	50
TiCl_3 solution	$0.25 \text{ g cm}^{-3} \times 0.50 \text{ cm}^3$ (0.13 g) ^c	100

a. $0.40 \mu\text{g cm}^{-3}$.

b. Optimum amount.

c. Absolute amount.

1200 rpm, at least 4-min of stirring was required to achieve equilibrium. Thus, 5-min of stirring was selected.

Optimization of the conditions for the determination of nitrate and nitrite nitrogens

For the determination of nitrate and nitrite nitrogens, these analyte ions should be reduced to ammonium ion prior to the determination. Therefore, various reducing agents to convert the analyte ions into ammonium ion were tested. The reducing agents examined here were zinc powder, aluminum powder, Devarda's alloy, tin(II) chloride solution and titanium(III) chloride solution. Each reduction efficiency with the respective optimum added amount of the agents was compared. The efficiency was derived from the ratio of the absorbance of ammonia produced from a nitrate to that obtained from an ammonium standard solution with the same nitrogen concentration. Table 1 gives these results. Metallic reducing agents, such as zinc, aluminum, and Devarda's alloy, gave poor reducing efficiencies, possibly due to their inhomogeneous dispersion.

Furthermore, hydrogen bubbles were generated when these metals were dissolved in a strongly basic solution. Aqueous mists were entrained with the hydrogen and the

Fig. 5 Effect of the titanium(III) chloride concentration on the reduction of nitrate and nitrite ions. Δ , ammonium ion; $\circ$, nitrate ion; $\blacksquare$, nitrite ion; mixing time, 5 min; ammoniacal, nitrate or nitrite nitrogen, $0.40 \mu\text{g cm}^{-3}$.

carrier gas to introduce into the cell, which also caused spectral interference. By using the titanium(III) chloride solution, a quantitative reduction of nitrate and nitrite ions to ammonium ion was achieved, while reduction by a tin(II) chloride solution was not complete to produce ammonium ion.

As for nitrite ion, a quantitative reduction to ammonium ion was also observed using a titanium(III) chloride solution. Therefore, the effect of the concentration of titanium(III) chloride on the reduction of nitrate and nitrite ions was examined according to the recommended procedure. When each concentration of nitrate or nitrite nitrogen was kept at less than $0.8 \mu\text{g cm}^{-3}$ it was sufficient for the complete reduction to ammonium ion; the concentrations of the titanium(III) chloride were 80 mg cm^{-3} and 60 mg cm^{-3} for nitrate and nitrite ions, respectively. Furthermore, essentially the same sensitivity of nitrogen derived from nitrate, nitrite and ammonium ions was obtained when a titanium(III) chloride solution was employed (Fig. 5).

Table 2 Effect of foreign ions on the determination of ammoniacal and nitrate nitrates

Ion	[Ion]/[N] weight ratio	Recovery, %	
		Ammoniacal nitrogen ^a	Nitrate nitrogen ^b
None	—	100	100
Na^+	1000	98	99
K^+	100	100	100
Mg^{2+}	100	99	100
Ca^{2+}	100	100	100
Fe^{2+}	100	100	97
Cu^{2+}	100	100	100
Pb^{2+}	100	100	99
CO_3^{2-}	100	98	100
SO_4^{2-}	100	99	98
S^{2-}	100	100	91
Cl^-	1000	101	99

a. Ammoniacal nitrogen $0.40 \mu\text{g cm}^{-3}$.

b. Nitrate nitrogen $0.40 \mu\text{g cm}^{-3}$.

Interference study

According to the recommended procedures, the effect of common foreign ions on the determination of ammoniacal and nitrate nitrates was examined. As Table 2 shows, foreign ions at the concentration levels tested here produced no interference. The proposed method would be suitable for determining inorganic nitrogen in samples, such as river and industrial-effluent water samples.

Analytical performance

Calibration graphs were established by the proposed method with 30-cm^3 aliquots of ammonium, nitrate or nitrite standard solution. The graphs were linear through the origin within the concentration range of $0.8 \mu\text{g cm}^{-3}$ of nitrogen with essentially the same slope, and correlation coefficients (r) of 0.98, 0.97 and 0.98 for ammonium, nitrate and nitrite ions, respectively. The same detection limit ($3S/N$) of $0.01 \mu\text{g cm}^{-3}$ of nitrogen was obtained for ammonium, nitrate and nitrite ions.

Table 3 Analytical results of ammoniacal, nitrate and nitrite nitrates in river and industrial water samples

Sample	Ammoniacal nitrogen/ $\mu\text{g cm}^{-3}$		Nitrate and nitrite nitrogen/ $\mu\text{g cm}^{-3}$	
	Proposed method	JIS method ^a	Proposed method	JIS method ^b
Suetake River	0.19 ± 0.01	0.19 ± 0.02	0.05 ± 0.01	0.05 ± 0.01
Nisiki River	0.28 ± 0.02	0.26 ± 0.02	0.08 ± 0.01	0.08 ± 0.01
Industrial water	<0.01	<0.01	0.18 ± 0.01	0.20 ± 0.01
Industrial water ^{c,d}	0.40 ± 0.02	—	0.56 ± 0.04	—
Industrial water ^{c,e}	0.40 ± 0.02	—	0.57 ± 0.05	—
Industrial water ^{d,e}	<0.01	—	0.95 ± 0.07	—

a. Indophenol Blue spectrophotometry. b. Copper-cadmium column reduction-*N*-(1-naphthyl)ethylenediamine spectrophotometry. c. Ammoniacal nitrogen added, $0.40 \mu\text{g cm}^{-3}$. d. Nitrite nitrogen added, $0.40 \mu\text{g cm}^{-3}$. e. Nitrate nitrogen added, $0.40 \mu\text{g cm}^{-3}$.

The relative standard deviations for five replicate measurements were 3.9, 4.5 and 4.7% for $0.4 \mu\text{g cm}^{-3}$ of nitrogen in the forms of ammonium, nitrate and nitrite ions, respectively. Eight samples could be analyzed per hour.

Application to practical samples

The accuracy of the proposed method was estimated by analyzing several samples. The results obtained by the calibration method are listed in Table 3 and are in good agreement with those analyzed by the methods according to the Indophenol Blue and the copper-cadmium column reduction-*N*-(1-naphthyl)ethylenediamine spectrophotometries.¹ Compared to these JIS methods, the proposed method requires no distillation procedure, which allows rapid analysis.

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