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Abstract

We developed capillary zone electrophoresis (CZE) with direct UV detection for determination of ammonium in environmental water samples. Ammonium in the samples was partly converted into ammonia in the alkaline background electrolyte (BGE) during migration and was detected by molecular absorption of ammonia at 190 nm in approximately 7 min. The limit of detection (LOD) for ammonium was 0.24 mg/l (as nitrogen) at a signal-to-noise ratio of three. The respective values of the relative standard deviation (RSD) of peak area, peak height, and migration time for ammonium were 2.1, 1.8, and 0.46%. Major alkali and alkaline earth metal ions coexisting in the samples did not interfere with ammonium determination by the proposed method. The proposed method determined ammonium in surface water and sewage samples. The results were compared to those obtained using ion chromatography (IC).

Keywords: Water analysis; Direct UV detection; Alkaline background electrolyte; Ammonium; Ammonia

1. Introduction

According to the annual report on the present environmental conditions in Japan [1], respective achievement ratios of environmental criteria for biochemical oxygen demand (BOD) in rivers and chemical oxygen demand (COD) in lakes during 1998–2002 have been almost constant: ca. 80% and 40%. This fact suggests that eutrophication has been progressing in water environments. It is also known that if the concentration of ammonia nitrogen in river waters is high, the disinfectant effect of chlorine for the production of drinking water will become insufficient because most chlorine would thereby be consumed for decomposition of the ammonia nitrogen. Furthermore, ammonia can inhibit bromate formation in ozonated drinking water [2]. Toxicity of ammonia to the zooplankton community and freshwater amphipods is also reported [3, 4]. Moreover, ammonium in drinking water is readily transformed into nitrate, which is reportedly toxic for human beings [5]. It is therefore important to determine ammonium in environmental waters.

Ammonium in environmental waters is generally determined by indophenol blue spectrophotometry [6]. Other methods include, flow injection analysis (FIA) [7-9], ion chromatography (IC) [10], enzymatic method [11], spectrophotometry [12, 13], sequential injection analysis (SIA) [14, 15], and gas chromatography (GC)-mass spectrometry (MS) [16]. Recently, a high-capacity cation-exchange column was developed to provide better resolution of ammonium from sodium for IC analysis of environmental waters [17]. Mori et al. [18] described sensitive and rapid IC method to determine ammonium in rain and river waters. However, the baseline separations of ammonium from alkali and alkaline earth metal ions in real

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water samples were unobtainable. Fernandes et al. [19] proposed a unique FIA method with a light-emitting diode based photometer for simultaneous determination of ammonium and phosphate in natural waters. Quite recently, Moliner-Martínez et al. [20] demonstrated the usefulness of solid-phase extraction coupled to diffuse reflectance spectroscopy for determination of ammonium in water samples. Meseguer-Lloret et al. [21] developed an HPLC method with chemiluminescence detection after derivatization of ammonium using dansyl chloride.

Capillary zone electrophoresis (CZE) has been applied to determination of inorganic ions in environmental waters [22]. Indirect UV detection is generally used for CZE determination of ions that have no UV absorbance such as alkali and alkaline earth cations including ammonium [23]. Alternatively, sensitive and universal conductivity detection was applied to simultaneous determination of anions and cations by CZE [24]. When using the above detection systems, however, high concentrations of coexisting inorganic cations might interfere with determination of ammonium in environmental waters. For example, it is difficult to separate ammonium from potassium without using the interaction between potassium and 18-crown-6. For that reason, it is worthwhile to develop other detection systems for CZE determination of ammonium in environmental waters. It is also known that ammonia has molecular absorption even though ammonium has no UV absorbance. Nakamoto et al. [25] determined total inorganic and ammonical nitrogens in water using gas-phase molecular-absorption spectrometry (GPMAS). Haghighi et al. [26] also described FIA-GPMAS for sequential determination of ammonium and nitrate in spiked water samples.

The present study developed a CZE procedure for direct determination of ammonium in environmental waters using molecular absorption of ammonia. The following analytical conditions were examined: effects of pH of background electrolyte (BGE), wavelength for detection, applied voltage, injection period of a sample solution, and concentration of matrix ions. The proposed method was applied to determination of ammonium in river and sewage waters. The results were compared to those obtained by IC.

2. Experimental

2.1. Apparatus

The capillary electrophoresis (CE) apparatus used throughout this study had a UV-visible absorbance detector (270A-HT; Perkin-Elmer, Foster City, CA, USA). A polyimide-coated fused-silica capillary electrophoresis column was used (100 μm I.D. × 375 μm O.D; GL Sciences, Tokyo, Japan). Total length of the column (L_{tot}) was 72 cm; its effective length (L_{det}) was 50 cm. Peak area, peak height, and migration time were measured using a Chromato-Integrator (D-2500; Hitachi, Tokyo, Japan). This experiment used an ion chromatograph (Model DX-AQ1211 V; Dionex, Sunnyvale, CA, USA) with a cation pre-column (CG12; Dionex), a cation separator column (CS12; Dionex), a suppressor (CSRS-I; Dionex), and a conductivity detector. The same integrator as that used for CZE was employed for integration.

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2.2. Reagents

All reagents were of analytical-reagent grade and were used as received. Standard solutions containing 0–5.0 mg/l ammonium were used for examination of analytical conditions; calibration graphs were prepared from 1000 mg/l ammonium chloride (Wako Pure Chemical Industries, Osaka, Japan). Ammonium concentration was expressed as nitrogen concentration. Sodium borate (Nacalai Tesque, Kyoto, Japan) and sodium hydroxide (Nacalai Tesque) were used to prepare BGE. Methanesulfonic acid (Aldrich Chemical, Milwaukee, WI, USA) was used to prepare the mobile phase of the IC method. Distilled, demineralized water, obtained from an automatic still (WG220; Yamato Kagaku, Tokyo, Japan) and a Milli-QII system (Nihon Millipore, Tokyo, Japan), were used for all experiments. Surface water samples were taken directly from the respective river surfaces in 100-ml polypropylene bottles (Sanplatec, Osaka, Japan). Sewage samples were taken from the inlet and outlet sites at a sewage treatment works near our university. All solutions used in this study, including surface water and sewage samples, were filtered through a 0.45-μm membrane filter (Advantec Toyo Kaisha, Tokyo, Japan) before use.

2.3. Procedure

Ammonium in the samples was determined by the following procedure within the day when the samples were collected. A sample was filtered through a 0.45-μm membrane before analysis. No pretreatment procedures were required except for

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filtration. The detection wavelength was set at 190 nm for CZE determination of ammonium. The thermostat was maintained at 30 °C. A new capillary was washed with 1 M sodium hydroxide for 40 min and then with water for 10 min. The capillary was filled with BGE (20 mM borate adjusted to pH 10 with 1 M sodium hydroxide) by vacuum for 3 min. A sample was vacuum injected into the CE apparatus for 5 s (325 nl). The injection period of 1 s corresponds to the sample volume of 65 nl. A voltage of 10 kV was applied with the sample inlet side as the anode. Each step was run automatically. Calibration graphs were prepared using synthetic standards.

3. Results and discussion

3.1. pH of BGE

It is considered that the molecular absorption of ammonia is caused by the transition of an electron in n-orbital to σ* orbital [27]. An alkaline BGE must be used considering from the acid dissociation constant (pK_a=9.24 [28]) of ammonium to use the molecular absorption of ammonia for CZE determination of ammonium. Therefore, the pH of 20 mM sodium borate solution was varied in the range of 8–11 using 1 M hydrochloric acid or 1 M sodium hydroxide. A sample solution containing 5.0 mg/l ammonium was analyzed by the procedure to examine the effect of pH of the BGE. Figure 1 illustrates the results. The values on the ordinate show the ratios of the peak area and peak height for ammonium to those obtained using the BGE with pH 8. The peak area increased concomitant with increased pH

up to pH 10; then it almost leveled off. The peak height also increased linearly with increasing pH of the BGE up to 11. However, an unstable baseline with higher noise was observed when the BGE with pH 11 was used. On the other hand, the migration time increased linearly with an increase in the BGE pH. The effective mobility for ammonium decreased because the higher the BGE pH, the larger the ratio of ammonia to ammonium. The BGE with pH 10 was adopted in subsequent experiments based on the results described above.

3.2. Wavelength for detection

According to the published papers, 201 nm [25] or 194 nm [26] was used as the wavelength for the ammonia molecular absorption. The effect of wavelength on peak area and peak height for ammonium was studied over the range of 190–205 nm. The sample containing the same concentration of ammonium as that used in Section 3.2 was analyzed using the BGE with pH 10. Figure 2 shows that both the peak area and peak height for ammonium decreased with an increase in wavelength. Values on the ordinate show the ratios of the peak area and peak height for ammonium to those obtained using the wavelength of 190 nm. No ammonium peak was observed when the wavelength was 205 nm. Both the ratios for 190 nm were three times larger than those for 195 nm. In general, the baseline noise that restricts the limit of detection (LOD) is serious at shorter wavelength. However, the noise level for 190 nm was almost equal to that for 195 nm with the analytical conditions used in this study. Therefore, 190 nm was adopted as the wavelength for ammonium determination.

3.3. Applied voltage

The effects of applied voltage on peak area, peak height, and migration time for ammonium were investigated using the applied voltage of 6–14 kV. Both the peak area and migration time for ammonium decreased linearly with increasing applied voltage, whereas the peak height was approximately constant. The relative standard deviation (RSD) of the peak height for ammonium was 3.1%. The RSD was calculated using five values of the average peak height of three determinations for each voltage. The unstable baseline with higher noise was also obtained when the applied voltage was greater than 10 kV. Taking into account the shorter analysis time and the lower baseline noise, 10 kV was adopted as the optimal voltage for ammonium determination.

3.4. Injection period of a sample solution

The sample-solution injection period used in the previous sections was varied in the range of 3–7 s. Both the peak area and peak height for ammonium increased linearly concomitant with the increasing injection period. However, baseline separation of ammonium and water dip observed after the ammonium peak was not obtained when the injection period was longer than 6 s. The migration time for ammonium, on the contrary, decreased with an increase in injection period. It was presumed that the decrease of the migration time occurred because the increased amount of water intensified the field strength in the capillary. Consequently, the optimal injection period for a sample solution was 5 s (325 nl). The volume of 325

nl occupies 5.7% of the capillary. In practice the volume of sample that can be injected in normal circumstances is 1-2% of the capillary volume because larger volumes will result in deterioration in the quality of the separation [29]. The volume of sample (5.7% of the capillary) appeared to be larger than that for a normal injection mode. In the proposed method, ammonium migrates faster in the sample zone than in the BGE because dominant species in the sample zone and the BGE are ammonium and ammonia, respectively. Therefore ammonium was presumably stacked at the sample-BGE interface according to the similar phenomenon observed in dynamic pH junction [30].

3.5. Effect of matrix in a sample solution

The electrophoretic mobility of ammonium is generally similar to that of potassium in an ordinary BGE. However, based on the migration time mentioned in Section 3.1, we presumed that ammonium mobility is smaller than potassium mobility in the proposed BGE. In addition, potassium has no UV absorbance. Therefore, it was expected that coexisting potassium in a sample scarcely interfered with ammonium determination by the proposed method. The concentration of potassium in river waters is generally 2.3 mg/l [31]. Sample solutions containing 3.0 mg/l ammonium and 0–10 mg/l potassium were analyzed by the method to confirm this prediction. The potassium concentrations in the sample solutions were different, but the peak area, peak height, and migration time for ammonium were approximately constant. The respective RSDs of peak area, peak height, and migration time for ammonium were 1.6, 1.5, and 1.3%. The RSD values were

calculated similarly to those in Section 3.3. No interference of potassium was verified. According to the above results, it was also predicted that other major cations coexisting in river waters such as sodium, magnesium, and calcium rarely interfered with ammonium determination. The following experiment was carried out to confirm the prediction. The concentrations of sodium, magnesium, and calcium in river waters are generally 9, 4, and 1.5 mg/l [31]. Sample solutions containing 3.0 mg/l ammonium and 0–90% volume of real river water were prepared and analyzed. Ammonium was not detected in this river water by the proposed method prior to this experiment. Similarly, the peak area, peak height, and migration time for ammonium were approximately constant, as expected from the lack of UV absorbance of alkali and alkaline earth metal ions. The respective RSDs of peak area, peak height, and migration time for ammonium were 3.2, 1.7, and 3.1%. The major cations such as sodium, magnesium, and calcium did not either interfere with ammonium determination by the proposed method.

3.6. Calibration graphs

Calibration graphs for ammonium were linear using both peak area and peak height. Regression equations relating area and height responses to concentration for ammonium (x, 0–5.0 mg/l) were $y = 6.67 \times 10^3 x - 325$ (correlation coefficient, 0.9990) and $y = 8.75 \times 10^2 x + 268$ (0.9924), respectively. Table 1 summarizes RSDs and LODs for ammonium using the proposed direct UV detection and an indirect UV detection method. The theoretical plates for the proposed method were 7.5 times more numerous than those for the indirect detection method, even though

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the respective precisions and the LODs were similar. The larger theoretical plates for the proposed method was probably caused by the sample stacking described in Section 3.4. Table 2 summarizes LODs of determination of ammonium for the previously reported methods. The LOD for ammonium in our method was superior to the LODs in the SIA methods [14, 15] and the FIA-GPMAS method [26], but inferior to the LODs of all other methods.

3.7. Applications

The proposed method was applied to determination of ammonium in river water samples taken from the surface of the rivers around our university. The river water samples were also analyzed using IC method. Table 3 summarizes those results. The ammonium concentrations obtained by CZE were higher than those obtained by IC, especially in the sample taken from the Shuku River. Insufficient separation of ammonium from high concentration of sodium by the IC method is probably responsible for the difference. It is known that the ion chromatographic separation of adjacent sodium and ammonium peaks with higher concentration ratios is not feasible using ordinary separation columns [32]; better separation is obtainable using a newly developed column [17]. Figures 3(A) and 3(B) respectively depict an electropherogram and ion chromatogram of surface water from the Yamato River. A sharp ammonium peak was obtained with complete separation from the water dip by the CZE method. However, a perfectly baseline-separated ammonium peak from the sodium peak was not obtained by the IC method even though the sample was diluted 10 times. Table 2 shows analytical

results for ammonium in river waters reported in the papers published thus far. The ammonium concentration (0.44 mg/l) in the Shuku River was similar to that reported in other papers [12, 19, 20], but that (4.3 mg/l) in the Yamato River was much higher than the reported ammonium concentrations. The Yamato River has been one of the most polluted rivers in Japan. For example, the BOD value was 5.4 mg/l in the lower reaches of the Yamato River in 2003 according to the official announcement by Environment Agency Government of Japan (http://www.env.go.jp/water/suiiki/h15/index.html). The proposed method was also applied to determination of ammonium in inlet and outlet sewage samples taken from the sewage treatment works near our university. Table 4 shows that analytical results obtained using the calibration graph almost agreed with those obtained by the standard addition method.

Aliphatic amines also have UV absorbance around 200 nm [33]. Even if certain concentrations of aliphatic amines are present in river water samples, they probably do not interfere with the measurement of ammonium by the proposed method. In general, aliphatic amine concentrations in river waters are much lower than ammonium concentrations. For example, Gibb et al. [34] described that, "In each case, ammonia was the dominant species – occurring at concentrations between one and three orders of magnitude greater than those of any methylamines." In addition, Mishra et al. [16] reported, "River water samples showed the presence of 70 μg/l of diethylamine." The LOD for the proposed method was not sufficiently low to be affected by such low concentrations of aliphatic amines. It is necessary to examine the effects of aliphatic amines when further improvement of the LOD will be conducted.

4. Conclusions

We developed a CZE method with direct detection for determination of ammonium in environmental waters. The proposed method appears to be a promising alternative method for determination of ammonium in river waters and other sites that contain relatively high concentrations of ammonium. Further improvement of the LOD is desirable for lower concentrations of ammonium to make the method more useful. Ammonium concentrations are lower than the LOD of the proposed procedure in most river waters except for heavily polluted areas. It is considered that transient isotachophoresis [35] is a feasible online concentration procedure to improve the LOD for ammonium. It is also worthwhile to modify the proposed method for determination of ammonium in highly saline samples such as seawater.

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Fig. 1. Effect of pH of background electrolyte on peak area (empty bars) and peak height (filled bars) for ammonium. a, peak area; a_8, peak area for pH 8; h, peak height; h_8, peak height for pH 8. Electrophoretic conditions: capillary, L_{tot}=72 cm, L_{det}=50 cm, 100 μm I.D. × 375 μm O.D.; BGE, 20 mM sodium borate adjusted to pH 8–11 with 1 M hydrochloric acid or 1 M sodium hydroxide; voltage, 10 kV; wavelength for detection, 190 nm. Sample, 5.0 mg/l NH_4^+-N; vacuum injection period, 5 s (325 nl).

Fig. 2. Effect of wavelength on peak area (empty bars) and peak height (filled bars) for ammonium. a, peak area; a_{190}, peak area at 190 nm; h, peak height; h_{190}, peak height at 190 nm. Electrophoretic conditions except for pH (=10) of the BGE, sample, and vacuum injection period are as those shown in Fig. 1.

Fig. 3. (A) Electropherogram of surface water from the Yamato River. Electrophoretic conditions and vacuum injection period of the sample are as those shown in Fig. 1. Peaks: b=NH_4^+; f=H_2O. (B) Ion chromatogram of the same sample. Ion chromatographic conditions: mobile phase, 20 mM methanesulfonic acid; flow rate, 1.0 ml/min; detection, conductivity. Injection volume of the sample, 25 μl. Peaks: a=Na^+; b= NH_4^+; c=K^+; d=Mg^{2+}; e= Ca^{2+}.

Fig. 1

Fig. 2

Wavelength, nm
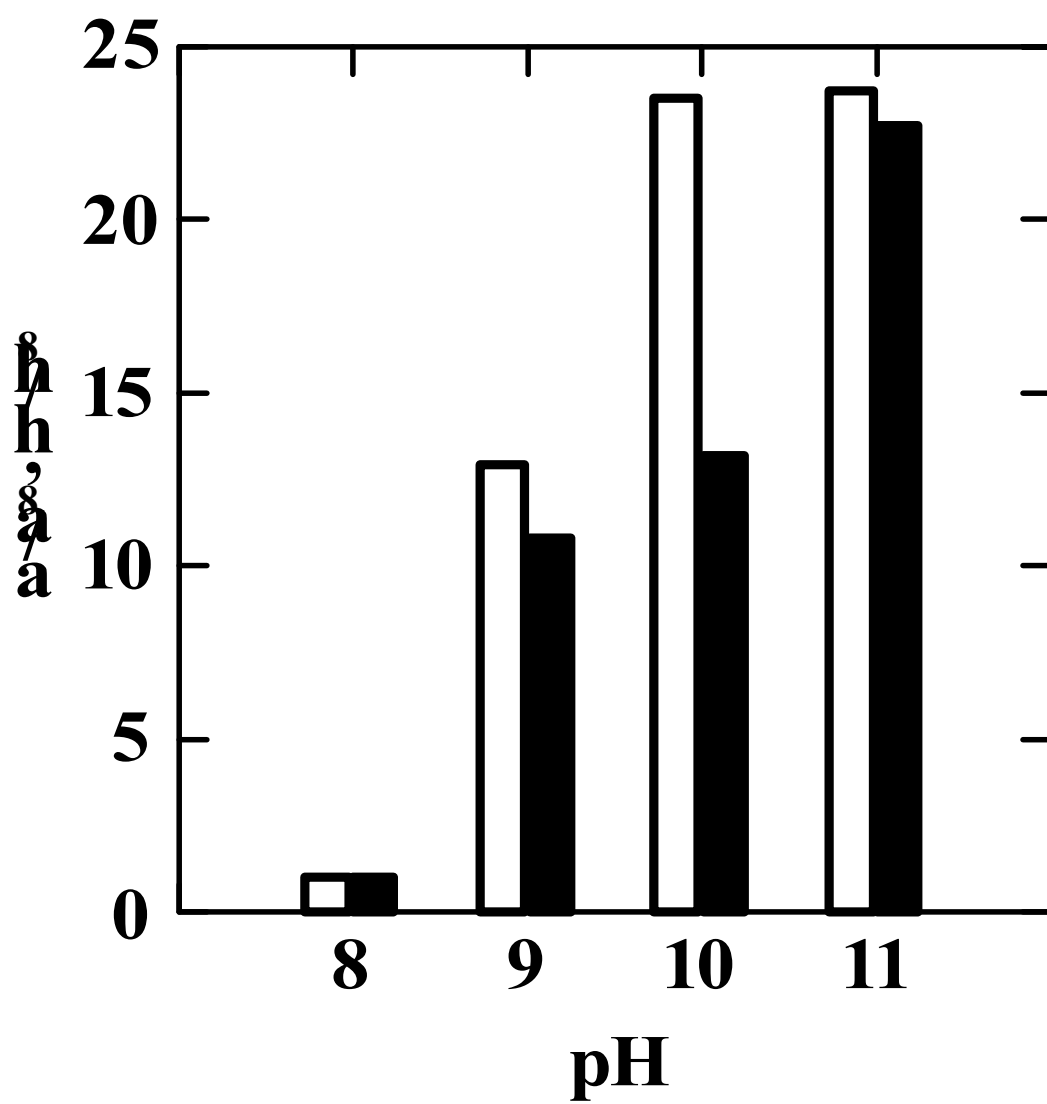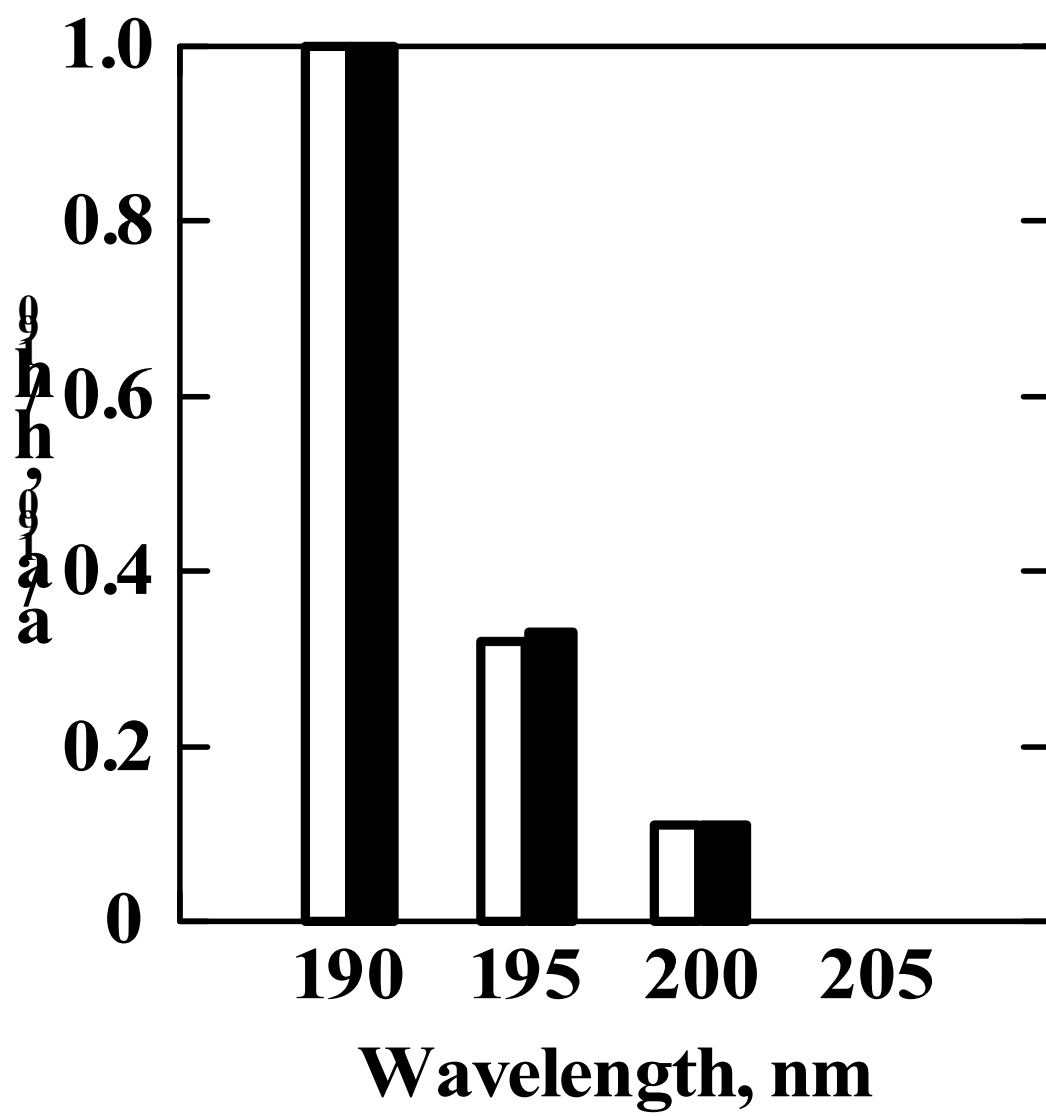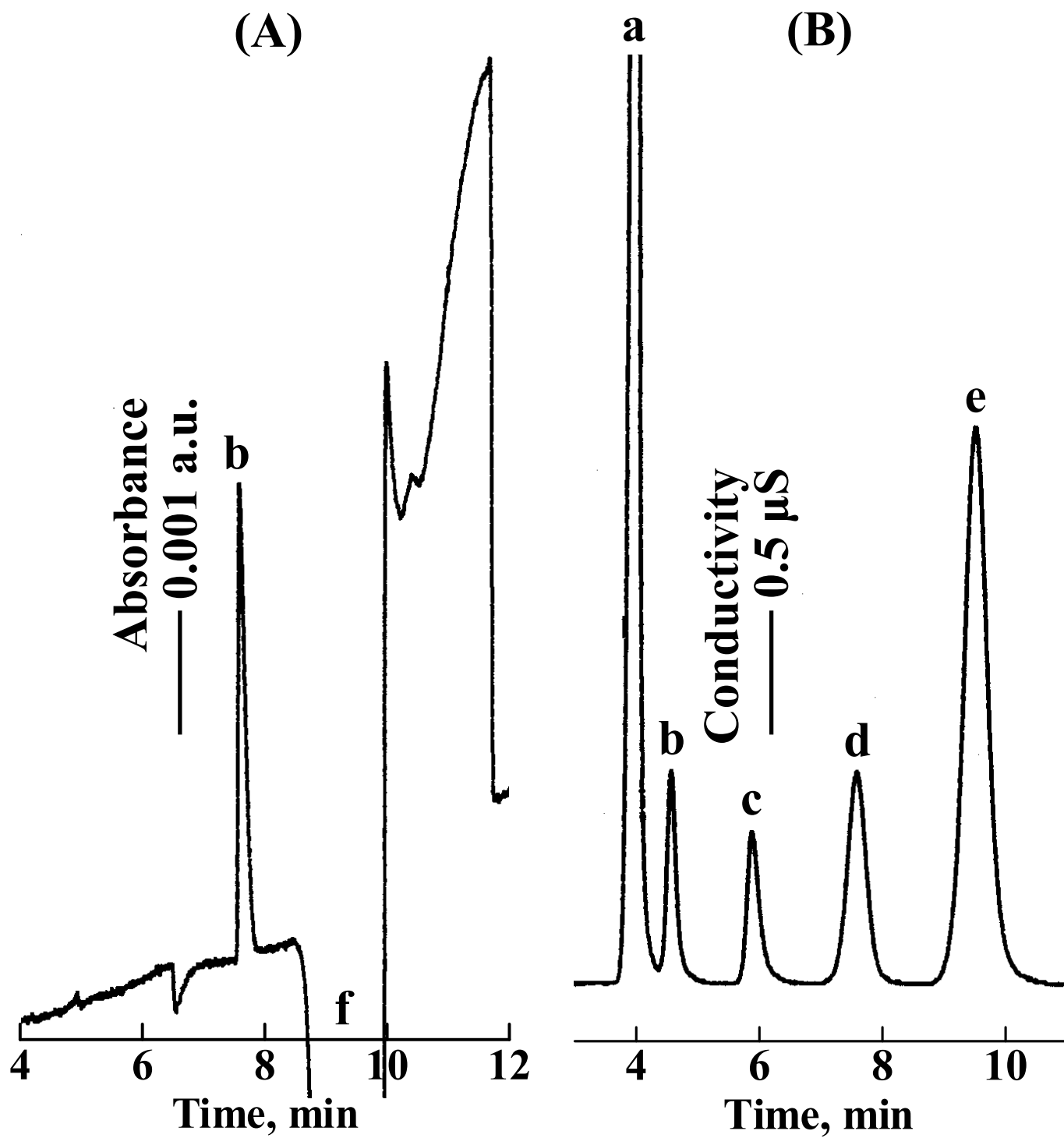
Fig. 3

Table 1

Precision and detection limits of determination of ammonium and efficiency in direct and indirect UV detection

	RSD[a] (%)			LOD (S/N=3)	Plate number
	Area	Height	Time	(mg/l)	
Direct UV[b]	2.1	1.8	0.46	0.24	30000
Indirect UV[c]	3.1	0.93	0.97	0.20	4000

[a]Sample: 3.0 mg/l NH_4^+-N, eight determinations.

[b]Electrophoretic conditions are as those shown in Fig. 1.

[c]Electrophoretic conditions: BGE, a mixture of 4.0 mM copper sulfate, 4.0 mM formic acid, and 3.0 mM 18-crown-6; other electrophoretic conditions as in the direct UV detection.

Table 2

Detection limits of determination of ammonium in published papers and concentration range of ammonium in river waters

LOD (mg/l, NH_4^+-N)	Definition	Methods	Concentration of NH_4^+ in river waters (NH_4^+-N, mg/l)	References
0.24	S/N=3	CZE with direct detection	0.44–4.3	Proposed method
		FIA-fluorometry	0.0054–0.151	[7]
		FIA-potentiometry	0.11–0.25[a]	[8]
0.001[a]	Three times the standard deviation of the blank	FIA-spectrophotometry		[9]
		IC	0.008–0.21[a]	[10]
0.0041	Twice the standard deviation of the blank	Enzymatic method		[11]
0.10[a]		Spectrophotometry using cryptand (2.2.2)	0.51–0.90[a]	[12]
0.0004[a,b]		Solid-phase spectrophotometry	0.0084–0.041[a,b]	[13]
0.39–1.6[a]	Five times the standard deviation of the blank	SIA with a gas-diffusion technique		[14]
0.36		SIA with an indophenol blue method		[15]
0.016[a,b]		GC-MS after solid-phase extraction		[16]

0.004[a]	Method detection limit determined using US Environmental Protection Agency method 300.0	IC		[17]
0.00693[a]	S/N=3	IC	1.6[a]	[18]
0.0054[a]		FIA with light-emitting diode based photometer	0.08–0.45[a]	[19]
0.0078[a]	Three times the standard deviation of the blank	Solid-phase extraction coupled to diffuse reflectance spectroscopy	0.032–0.78[a]	[20]
0.006[a]	S/N=3	HPLC with chemiluminescence detection after derivatization		[21]
0.0008–0.004[a]	S/N=3	CZE with conductivity detection		[24]
0.01[b]	S/N=3	GPMAS	0.19–0.28[b]	[25]
6[a]	Three times the standard deviation of the blank	FIA-GPMAS		[26]

[a]Recalculated by the authors.

[b]NH_3-N.

Table 3

Analytical results for ammonium in river water samples

Sampling site	NH_4^+-N (mg/l)	
	CZE[a]	IC[b]
Yamato River	4.3	3.9[c]
Muko River	ND[d]	ND
Shuku River	0.44	0.16[e]
Miya River	ND	ND

[a]Electrophoretic conditions are as those shown in Fig. 1.

[b]Ion chromatographic conditions are as those shown in Fig. 3(B).

[c]Ten-times diluted before analysis.

[d]ND, not detected.

[e]Five-times diluted before analysis.

Table 4

Analytical results for ammonium in sewage samples[a]

	NH$_4^+$-N (mg/l)	
	WC[b]	SA[c]
Before treatment[d]	10.5	11.2
After treatment[e]	4.1	4.5

[a]Electrophoretic conditions are as those shown in Fig. 1.

[b]WC, working curve method.

[c]SA, standard addition method.

[d]Four-times diluted before analysis.

[e]Two-times diluted before analysis.