

Photometric Determination of Boron with Azomethine-H Using Simplified Two-channel Flow Injection Analysis

Shigeko Ozaki¹, Miki Tatsumi¹ and Eiko Nakamura^{1,2,*}

¹ Graduate School of Environment and Information Sciences, Yokohama National University,
79-7 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

² Faculty of Education and Human Sciences, Yokohama National University,
79-2 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

A flow injection analysis (FIA) for boron determination was studied using a compact and simple two-channel manifold. This method is based on the chromogenic reaction of borate with azomethine-H to form a yellow complex. The absorbance of the complex was measured at 405 nm. The chemical factors and FIA variables influencing the color development were examined. When a 0.5% (w/v) azomethine-H solution (pH 6.5) containing 1.5 % (w/v) ascorbic acid and 10 % (w/v) ammonium acetate was used as a reagent solution, the constant and maximum absorbance was obtained at a flow rate of 1.2 mL min⁻¹ and a reaction temperature of 40 °C. Under optimum conditions with 200 µL sample injection, the calibration graph was linear from 0.01 to 1.2 mg L⁻¹ of boron. The relative standard deviation was 0.99 % ($n = 9$) at the 0.2 mg L⁻¹ level. The detection limit and the determination limit were 0.011 (3σ) and 0.037 (10σ) mg L⁻¹, respectively. The sampling rate was 20 h⁻¹. The proposed FIA promises a simple and rapid method with high sensibility and precision for boron determination in aqueous samples.

Keywords boron determination, azomethine-H, soil solution, FIA

1. Introduction

The natural borate content of groundwater and surface water is usually small. But recently the borate content can be significantly increased as a result of wastewater discharges, because boron compounds are widely used in industrial applications. Boron causes some serious health and environmental problems. A small content of boron is required for certain metabolic activities, but the excess of boron inhibits plant growth and affects male reproductive organs in animals. When humans consume high boron-containing foods and water, they will become ill with nausea, vomiting, diarrhea, or blood clotting. Therefore, boron level in the environment is regulated. WHO guideline value for drinking water is 0.5 mg L⁻¹ as B [1]. Japanese water quality standard for drinking water and the environmental quality standards for groundwater, river water, and soil are 1.0 mg L⁻¹ as B [2-5].

Many analytical methods for boron determination have been studied. Inductively coupled plasma optical emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS) are also widely used for the analysis of boron in a variety of samples such as waters, soils, plants, and biological materials [6-12]. The ICP-AES and ICP-MS methods have an advantage over other methods in higher sensitivity, lower detection limits and simultaneous measurement of elements. But ICP systems need much higher equipment costs and running costs. In contrast, the spectrophotometry is commonly used with low instrumentation costs. Although well-known reagents to form the colored complexes with borate are carminic acid and curcumine, it is not desirable

to use them because of requiring concentrated sulfuric acid on the complex formation. Azomethine-H does not require strict reaction conditions. Spectrophotometric methods using azomethine-H are available for the boron determination in aqueous samples [6, 9, 13, 14]. But the formation of azomethine-H-boron complex is very slow [15]. It took 4 hours until the complete color development at pH 4.5 [16]. According to the standard methods, the mixture solution of borate and azomethine-H (pH 5.9) must be allowed to stand for 2 hours at 20 °C [6, 13]. Several methods using flow analyses such as flow injection analysis (FIA) [17-23], continuous flow analysis (CFA) [24, 25], and sequential injection analysis (SIA) [26] were proposed to overcome the disadvantage in slow reaction.

Fluorimetric flow systems based on the reaction of borate with chromotropic acid afford rapid determination of boron in ppb or sub-ppb level [27, 28]. Nevertheless, we selected the photometric detector because it was less expensive than not only spectrofluorimetric detector but also spectrophotometric detector. A simple and rapid method for boron determination was studied using a compact FIA manifold composed of small and inexpensive apparatus. FIA parameters such as pH and reagent concentrations were re-examined to optimize the conditions for the boron determination by this FIA. And then the proposed FIA method was applied to the determination of boron in soil solutions.

2. Experimental

2.1. Reagents

All the chemicals used were of analytical reagent grade. Water purified with deionization and distillation was used for all experiments. A stock standard solution of 1.00 mg L^{-1} as B was prepared by diluting a commercial standard solution (Boron Standard Solution "B1000", Wako Pure Chemical Industries, Ltd., Japan) with water. The working standard solutions were prepared by diluting the stock standard solution with water using a series of 10 or 25 mL one-mark volumetric flasks. 8-*N*-(2-Hydroxybenzylidene)-amino-naphth-1-ol-3,6-disulfonic acid (azomethine-H) disodium salt (Dojindo Laboratories, Japan), L(+)-ascorbic acid (Junsei Chemical Co., Ltd., Japan), and ammonium acetate (Wako Pure Chemical Industries, Ltd., Japan) were used to prepare azomethine-H solutions. An azomethine-H solution (pH 6.5) for the proposed FIA method was prepared by dissolving 1.0 g of azomethine-H disodium salt, 3.0 g of L(+)-ascorbic acid, and 20 g of ammonium acetate in water and diluting to 200 mL with water in a one-mark volumetric flask on the day of use. A 2.0 g of EDTA disodium salt (Dojindo Laboratories, Japan) was added to the azomethine-H solution in order to mask metal ions.

2. 2. Soil solution

Collected soils were dried in air and their grain sizes were made smaller ($\leq 2 \text{ mm}$) by crushing and screening. A 50 g of soil was mixed with 500 mL of water (pH 6) and shaken continuously for 6 hours at 200 frequencies per minute using a shaking apparatus (Yamato Scientific, Co., Ltd., SA31, Japan). After the centrifugation of the mixture at 3,000 rpm for 20 minutes using a centrifuge machine (Tomy Seiko Co., Ltd., CD-50SN, Japan), the supernatant solution was filtrated through a $0.45 \mu\text{m}$ pore-size membrane filter. The filtrate given was used as soil solution for the boron determination [5].

2. 3. Apparatus

A flow injection system used is schematically shown in Fig. 1. A compact manifold (20 cm in width, 36 cm in height, and 25 cm in depth, OGAWA & Co., Ltd., model OG-FI-300S, Japan) was used. It consists of an all-in-one peristaltic pump, injector, thermostat, and photometric detector. This built-in detector equipped with flow cell (optical path-length = 1 cm), LED as light source, and photodiode was used to measure the absorbance. A recorder (Pantos Co., Ltd., Unicorder U-228) was used for monitoring of the absorbance-time response. Pharmed tubing (2.0 mm i.d.) was used for the peristaltic pump, and PTFE tubing (0.5 mm i.d.) was used for the injection loop and all manifold lines.

The carrier solution and the reagent solution were flowed

using a peristaltic pump. Sample or the working standard solution was injected into a carrier stream via a six-port injection valve. The carrier stream was merged with the reagent stream, and then borate reacted with azomethine-H in weak acid medium to form azomethine-H-boron complex in a reaction coil. The increase in absorbance by the complex formation was detected through a flow cell. The absorbance-time response was recorded to obtain the peak absorbance.

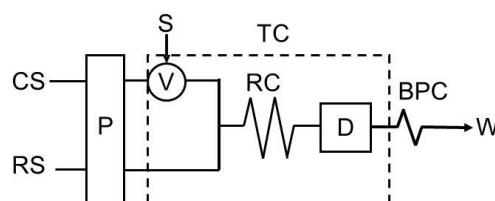


Fig. 1 Flow diagram for boron determination

CS, carrier solution (H_2O); RS, reagent solution (0.5 % azomethine-H solution (pH 6.5) containing 1.5 % ascorbic acid and 10 % ammonium acetate); P, peristaltic pump (1.2 mL min^{-1}); S, sample ($200 \mu\text{L}$); V, six-port injection valve; RC, reaction coil ($0.5 \text{ mm i.d.} \times 10 \text{ m}$); TC, thermostatic chamber ($40 \text{ }^\circ\text{C}$); D, photometric detector; BPC, back-pressure coil; W, waste.

A pH meter (DKK-TOA Co., Ltd., HM-25R, Japan) was used to adjust the pH of azomethine-H solutions. A UV-visible spectrophotometer (Shimadzu Co., Ltd., UV-1650PC, Japan) was used to measure the absorption spectra of azomethine-H solutions. An inductively coupled plasma optical emission spectrometer (ICP-AES, Shimadzu Co., Ltd., model ICPS-8000E, Japan) was also used to determine boron in soil solutions.

3. Results and discussion

3. 1. Azomethine-H-boron complex formation

We preliminarily measured the absorption spectra of azomethine-H solutions in the presence/absence of borate to examine the pH conditions for the azomethine-H-boron complex formation. Azomethine-H (0.12 %) solutions containing ascorbic acid (0.4 %) and ammonium acetate (5.2 %) were used. The pH of azomethine-H solutions were adjusted using acetic acid or ammonia. Absorption spectra of the azomethine-H solutions at various pH values are shown in Fig. 2. It shows that the pH conditions greatly affected the absorption spectra. Molecular structure of azomethine-H is shown in Fig. 3. It is considered that a shift in spectra as shown in Fig. 2 was due to the various forms such as H_4Azo , H_3Azo^- , $\text{H}_2\text{Azo}^{2-}$, HAzo^{3-} , and Azo^{4-} ($\text{pK}_{\text{a}2} = 5.7$, $\text{pK}_{\text{a}3} = 10.1$, and $\text{pK}_{\text{a}4} = 10.2$) [29]. Whereas the absorption bands between 400 and 420 nm at pH 5.5, 6.0, and 6.5 were relatively small, those at pH 7.0 and 7.5 were considerably larger. This is

considered because the H_2Azo^{2-} form of azomethine-H increased with a higher pH values.

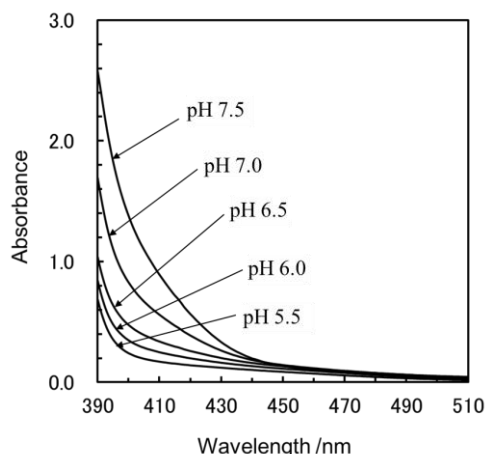


Fig. 2 Absorption spectra of azomethine-H solutions.

Azomethine-H solutions, 0.12% azomethine-H, 0.4 % ascorbic acid, and 5.2 % ammonium acetate; blank, water.

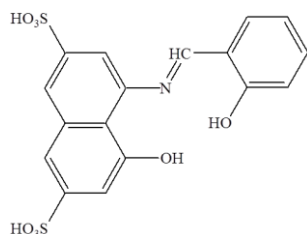


Fig. 3 Molecular structure of azomethine-H

Azomethine-H of a tetrabasic acid is expressed as H_4Azo ; four ionized species are expressed as H_3Azo^- , H_2Azo^{2-} , $HAzo^{3-}$, and Azo^{4-} , respectively.

Absorption spectra of the azomethine-H solutions in the presence of borate (0.60 mg L^{-1} as B) at various pH values are shown in Fig. 4.

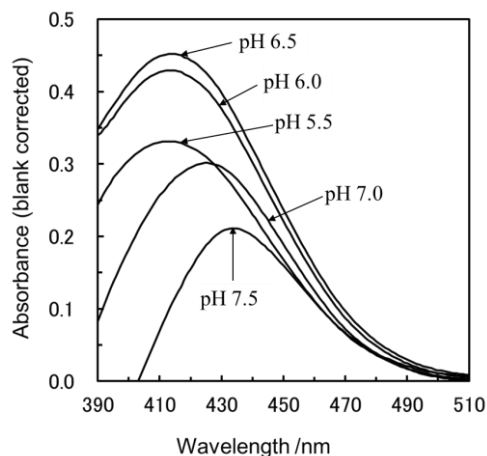


Fig. 4 Absorption spectra of azomethine-H solutions in the presence of borate (0.60 mg L^{-1} as B).

Azomethine-H solutions, 0.12% azomethine-H, 0.4 % ascorbic acid, and 5.2 % ammonium acetate; standing time, 2 hours in the dark at room temperature; corrected for reagent blank.

A yellow complex was formed through the reaction of azomethine-H with borate. The net absorbance corrected for reagent blank was correlated with the formation of azomethine-H-boron complex. Of five pH values studied, the peak value of the net absorbance at pH 6.5 was the highest. The wavelength of maximum absorption at pH 6.5 was 413 nm, and also those at pH 5.5 and 6.0 were 413 nm. The wavelengths of maximum absorption at pH 7.0 and 7.5 were 425 and 434 nm, respectively. A shift in the wavelength of maximum absorption is considered because of the shift in absorption spectra of azomethine-H solutions (Fig. 2).

3. 2. Optimization of the FIA parameters

The optimum conditions for the boron determination were examined using the FIA system as shown in Fig. 1.

3. 2. 1. Measuring wavelength

As shown in Fig. 4, a recommended measuring wavelength is 413 nm. Simple optical detector used in this FIA system has no capability to measure the absorbance spectrometrically. Therefore, a blue LED ($\lambda_{\text{max}} = 405 \text{ nm}$) with emission wavelength of nearly 413 nm was chosen as light source. In this study the absorbance was measured at 405 nm.

3. 2. 2. The pH of reagent solution (RS)

The effect of pH ranging from 5.5 to 7.5 on absorbance is shown in Fig. 5. High absorbance was obtained in the range of pH 6.0 to 6.5. The result shown in Fig. 5 corresponded to the results shown in Fig. 4. The acceleration of the complex formation observed in the pH 6.0-6.5 is considered to be caused by the effective deprotonation of azomethine-H [20, 29]. The maximum absorbance was at pH 6.5. Therefore, the pH value of reagent solution was adjusted at 6.5 using ammonium acetate in further experiments.

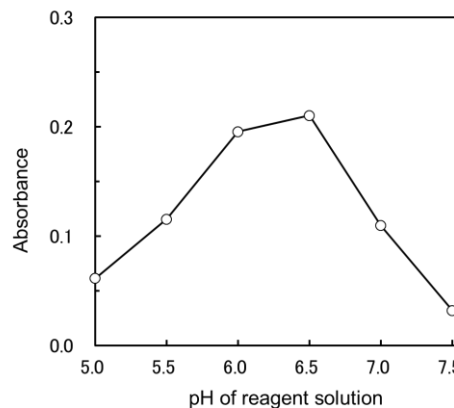


Fig. 5 Effect of pH on absorbance

B, 1.0 mg L^{-1} ; CS, H_2O ; RS, 0.5 % azomethine-H, 1.5 % ascorbic acid, 10 % ammonium acetate; flow rate, 1.2 mL min^{-1} ; injection volume, $200 \mu\text{L}$; RC, 10 m; temperature, $40 \text{ }^\circ\text{C}$.

3. 2. 3. Ammonium acetate concentration of RS

The effect of ammonium acetate concentration ranging from 0.8 to 30 % on absorbance was examined. The maximum and stable absorbance was obtained at more than 8 % concentrations. Therefore, ammonium acetate concentration of 10 % was chosen as optimum to be high buffer capacity.

3. 2. 4. Azomethine-H concentration of RS

The effect of azomethine-H concentration ranging from 0.1 to 0.7 % on absorbance is shown in Fig. 6. The absorbance values increased with an increase in the concentration of azomethine-H up to 0.45 % and then were constant at higher concentrations. However, at more than 0.8 % concentrations net absorbance values could not be obtained due to much larger reagent blanks. Therefore, azomethine-H concentration of 0.5 % was chosen as optimum.

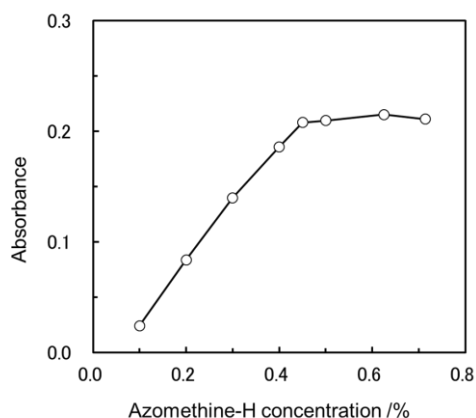


Fig. 6 Effect of azomethine-H concentration on absorbance B, 1.0 mg L⁻¹; CS, H₂O; RS, azomethine-H, 1.5 % ascorbic acid, 10 % ammonium acetate, pH 6.5; flow rate, 1.2 mL min⁻¹; injection volume, 200μL; RC, 10 m; temperature, 40 °C.

3. 2. 5. Ascorbic acid concentration of RS

Ascorbic acid was traditionally added to azomethine-H solutions in order to retard oxidation [15]. The effect of ascorbic acid concentration ranging from 0 to 3 % on absorbance was examined. The results show that the concentration of ascorbic acid did not affect the absorbance. Time-dependence of absorption spectrum of the azomethine-H solution prepared without ascorbic acid is shown in Fig. 7 and that of the azomethine-H solution prepared with ascorbic acid is shown in Fig. 8. The FIA method proposed by Nishioka et al. does not need the addition of ascorbic acid to the azomethine-H solution [19]. As shown in Fig. 7, even if stored in the refrigerator the azomethine-H solution without ascorbic acid became increasingly red-brown due to the formation of oxidative degradation products. As shown in Fig. 8, the azomethine-H solution with ascorbic acid was stable at least 5

days after the preparation. Ascorbic acid concentration of 1.5 % was chosen because the typical ratio of it to azomethine-H concentration is 3to1 [6, 13].

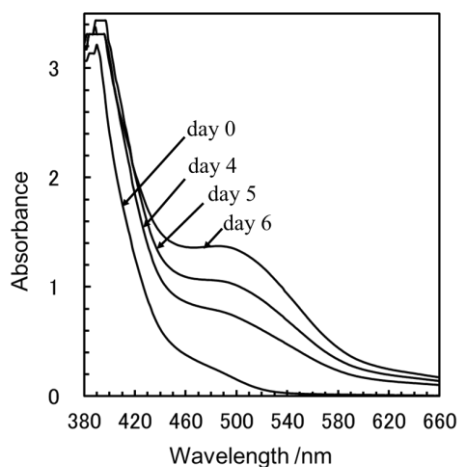


Fig. 7 Absorption spectra of azomethine-H solutions (0, 4, 5, and 6 days after the preparation) without ascorbic acid.

0.5 % azomethine-H, 10 % ammonium acetate, pH 6.5; stored in the refrigerator.

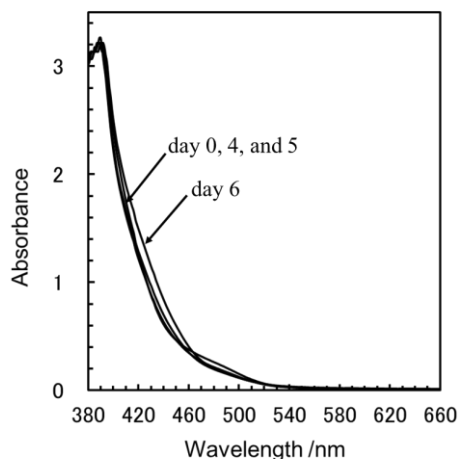


Fig. 8 Absorption spectra of azomethine-H solutions (0, 4, 5, and 6 days after the preparation) with ascorbic acid.

0.5 % azomethine-H, 1.5 % ascorbic acid, 10 % ammonium acetate, pH 6.5; stored in the refrigerator.

3. 2. 6. Flow rate

The relationship between the revolutions per minute of the peristaltic pump used (x , in rpm) and the flow rate (y , in mL min⁻¹) is given by the equation $y = 0.1683x$ ($R^2 = 0.9999$). The effect of flow rate ranging from 0.50 to 1.35 mL min⁻¹ (3.0-8.0 rpm) on absorbance was examined. The absorbance values gradually decreased with an increase in the flow rate. Within the range studied the maximum absorbance was obtained at flow rate of 0.5 mL min⁻¹, and it took about 5 minutes to obtain the peak signal. When the flow rate was 1.2 mL min⁻¹, it took about 2 minutes to obtain the peak signal (about 84 % of the maximum absorbance). In consideration of the sampling rate, the flow rate of 1.2 mL min⁻¹ was chosen.

3. 2. 7. Reaction temperature

The effect of reaction temperature ranging from 25 to 60 °C on absorbance is shown in Fig. 9. It is indicated that the reaction temperature have a significant influence on the formation of azomethine-H-boron complex. The decrease in absorbance appeared at more than 30 °C, and the rate of decrease became rising with higher temperature. The fact that the absorbance decreases as the temperature increases is explained due to thermolability of azomethine-H and/or the formed complex [20,29].

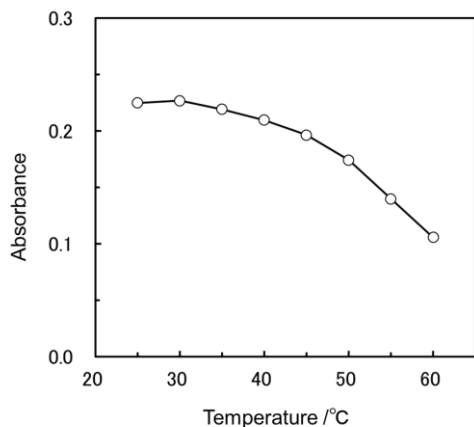


Fig. 9 Effect of reaction temperature on absorbance

B, 1.0 mg L⁻¹; CS, H₂O; RS, 0.5 % azomethine-H, 1.5 % ascorbic acid, 10 % ammonium acetate, pH 6.5; flow rate, 10 mL min⁻¹; injection volume, 200 μL; RC, 10 m.

3. 3. Analytical performance

The optimum conditions for the boron determination by this FIA method are shown in Table 1. The typical flow signals obtained under the optimum conditions are shown in Fig. 10.

Table 1 Optimum conditions for boron determination by this FIA method

Flow rate	1.2 mL min ⁻¹
Sample injection volume	200 μL
Temperature	40 °C
Reaction coil length	10 m
Wavelength	405 nm
Carrier solution	Water
Reagent solution	pH 6.5
Azomethine-H concentration	0.5 % (w/v)
Ascorbic acid concentration	1.5 % (w/v)
Ammonium acetate concentration	10 % (w/v)

The calibration graph was linear in the range of 0.01 to 1.2 mg L⁻¹ of boron. The calibration equation was $y = 0.1981x + 0.0021$ ($R^2 = 0.9997$) where x is boron concentration in mg L⁻¹ and y is absorbance. The relative standard deviations ($n = 9$) were 0.79 and 4.1 % at the 1.0 and 0.04 mg L⁻¹ levels, respectively. The detection limit and the determination limit

were 0.011 (3σ) and 0.037 (10σ) mg L⁻¹, respectively. This FIA method achieved lower determination limit than those given by other FIA methods using azomethine-H [19, 20]. The sampling rate was 20 h⁻¹.

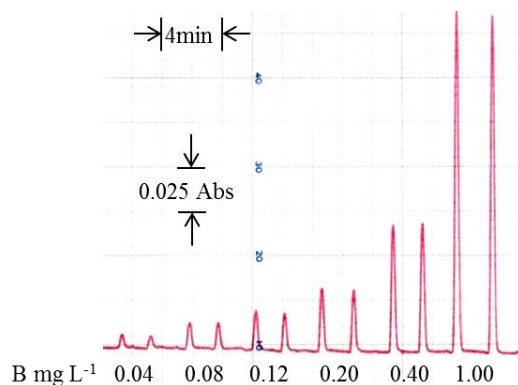


Fig. 10 Typical flow signals

obtained under optimum conditions as shown in Table 1.

3. 4. Application to boron determination in soil solution

3. 4. 1. Addition Effect of EDTA

The addition effect of EDTA was examined using a simulated soil solution. The simulated soil solution contains Al³⁺ (200 mg L⁻¹), Fe³⁺ (100 mg L⁻¹), Ca²⁺ (50 mg L⁻¹), Mg²⁺ (10 mg L⁻¹), Mn²⁺ (0.5 mg L⁻¹), and Zn²⁺ (0.5 mg L⁻¹). Of these metal ions, it is known that Mg²⁺, Zn²⁺, and Ca²⁺ did not interfere, but Mn²⁺, Fe³⁺, and Al³⁺ might cause high results [13]. The results are shown in Table 2. When the azomethine-H solution without EDTA was used, the foreign metal ions caused a significant error of plus in the boron determination. The error became smaller with an increase in additive amount of EDTA. Addition of 1.0 % EDTA made it possible to recover boron (1.0 mg L⁻¹) satisfactorily in the presence of Al³⁺ (200 mg L⁻¹) and Fe³⁺ (100 mg L⁻¹). Therefore, the azomethine-H solution with the addition of 1.0 % EDTA was used for determination of boron in soil solutions.

Table 2 Addition effect of EDTA on boron determination in the presence of foreign ions ^{a)}

Added EDTA, %	Recovery of B, %	Added EDTA, %	Recovery of B, %
0.0	966	0.7	148
0.2	856	1.0	99.6
0.5	218		

^{a)} Al³⁺, 200; Fe³⁺, 100; Ca²⁺, 50; Mg²⁺, 10; Mn²⁺, 0.5; Zn²⁺, 0.5; against B, 1.0; unit in mg L⁻¹.

3. 4. 2. Determination of boron in soil solution

The proposed FIA method was applied to the determination of boron in soil solutions. The loam and andosol solutions prepared as described in Section 2.2 were yellow-colored. A

sample blank was measured by pumping the solution prepared without azomethine-H in place of the azomethine-H solution into the reagent stream. The sample blanks for loam and andosol solutions were 0.0057 ± 0.0003 and 0.0173 ± 0.0002 , respectively ($n = 6$). Boron concentrations in the soil solutions were calculated using the absorbance values corrected for sample blanks. The results are shown in Table 3. Boron was not detected in the loam solution and trace amounts of boron were detected in the andosol solution. Satisfactory recoveries of boron (98-102 %) were found for recovery test using the soil solution. Additionally, these results obtained by the proposed FIA method were in agreement with those obtained by the official method (ICP-AES).

4. Conclusion

This method using an inexpensive and compact FIA system provides high sampling rate, sensitivity and precision, favorably comparing with FIA methods using conventional system. This method can be applied to determine boron at levels over 1/25 of Japanese environmental quality standards. This FIA method promises a simple and rapid method for monitoring the boron pollution of water, groundwater and soil.

Acknowledgement

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Table 3 Results for recovery test using the leaching solution from soils ^{a)}

Kind of soil	Added B, mg L ⁻¹	This FIA method		ICP-AES method [5, 6]	
		Found B, mg L ⁻¹ ^{b)}	Recovery of B, % ^{b)}	Found B, mg L ⁻¹ ^{b)}	Recovery of B, % ^{b)}
Loam	0.0	N. D.	—	N. D.	—
	1.0	1.01 ± 0.011	100 ± 1.4	1.00 ± 0.034	100 ± 3.4
Andosol	0.0	0.038 ± 0.002	—	0.016 ± 0.001	—
	1.0	1.01 ± 0.005	98 ± 0.3	1.03 ± 0.036	102 ± 3.6

a) taken at Yokohama National University b) mean value and standard deviation ($n = 3$)

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