

原著論文

FLOW INJECTION ANALYSIS OF ALKALINITY

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A flow-injection system (FIA) was described for the simple and rapid determination of alkalinity in fresh water. The method was based on the dependence of fluorescein's fluorescence intensity on pH, which was related to the concentration of alkalinity in the carrier solution.

The sample solution was injected into a flow system, which was comprised of reservoir, pump, line sampler, coil and fluorescence detector and the fluorescence intensity of the fluorescein was measured. The excitation and emission wavelength was 490 nm and 517 nm, respectively. The limit of determination was 0.5 mg/l of alkalinity as CaCO₃. A sampling rate was 80 samples per hour. The relative standard deviation was 4.5 %. The dominant constituents in natural water did not interfere the determination of alkalinity. The results by the proposed method agreed well with those obtained by the titration method.

[Key Words: Alkalinity, Flow injection analysis, fluorescein, Fluorometric detection]

1 INTRODUCTION

Alkalinity is a fundamental parameter of natural water, and the determination of alkalinity is useful for the control of physico-chemical and biological parameters in the treatment of natural water supplies. Recently, natural water acidification has become a serious environmental problem throughout the world. Acidification is monitored by means of measuring pH and alkalinity. Therefore, a rapid and simple method is important for the analysis of alkalinity in fresh water including drinking water, river water, and lake water. Alkalinity is a measure of the contents of weak bases (mainly bicarbonate ion, carbonate ion, and hydroxide compounds) and is most commonly measured by titration with strong acid⁽¹⁻³⁾. Other methods are also available, such as ion-selective electrode⁽⁴⁾, ion exchange⁽⁵⁾, ion-chromatography⁽⁶⁾, and gel chromatography. There is a growing demand for fast, automated measurement methods. F. Canete et al.⁽⁷⁾ reported an automated flow injection method based on the acid-base reaction and spectrophotometric detection. Other automated methods have also been reported⁽⁸⁻¹⁰⁾. This paper reports a method for the determination of alkalinity by means of a

FIA system employing a spectrofluorometric detector connected to a flow cell. This method was based on the pH dependency of fluorescein's fluorescence intensity in a carrier solution. Results using proposed method were compared with those obtained by the titration method.

2 MATERIALS AND METHOD

2 • 1 Reagents

The fluorescein disodium salt (uranine) used was of first reagent grade (Wako Chemicals). A fluorescein stock solution of 2.5×10^{-3} M was prepared by dissolving 0.94g of fluorescein disodium salt in one liter of distilled water. The carrier solution was prepared as follows: 1 ml of stock solution and 500 ml of 0.86 M sodium chloride solution were mixed, and the pH was then adjusted to 5.2 with 0.01 M hydrochloric acid solution, then the final volume was adjusted to 1000 ml. Standard alkalinity stock solution composed of CaCO₃ at 0.01 M (1060 mg/l) were prepared by dissolving 1.06g of sodium carbonate in 1000ml of distilled water. The exact concentration of alkalinity was determined by titration with 0.02 M H₂SO₄.

2 • 2 Apparatus

The system was comprised of the following components: a peristaltic pump (Atto Perista mini pump model SJ-1211 Japan), a line sampler (Kyowa Japan), and a fluorescence spectrophotometer (Simazu RF-530 Japan) equipped with a flow cell of 10 μ l. The diameter of the reaction coil (Teflon) was 0.8mm. The excitation and emission wavelengths were 490 nm and 517 nm, respectively. The analytical manifold is shown in Figure 1.

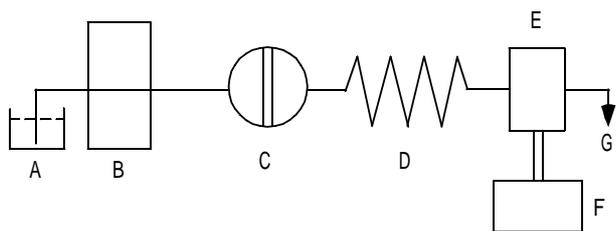


Fig.1 Manifold for the determination of alkalinity

A:Reservoir B:Pump C:Line sampler D:Coil
E:Fluorescence F:Detector F:Recorder G:Drain

2 • 3 Procedure

The carrier solution (pH 5.2) was pumped at flow rate of 1.5 ml/min. Five μ l of the sample was injected manually with a line sampler into the carrier stream. The increase in the emission intensity at 517 nm, owing to the dissociation of fluorescein by the alkalinity, was measured. The peak measured height can be related to the alkalinity concentration as CaCO_3 . The recommended conditions for the determination of alkalinity are listed in Table 1.

Table 1 Recommended conditions for determination of alkalinity by flow injection method

Conditions	Recommended condition
Coil length (m)	1.5
Flow rate (ml/min)	1
Concentration of carrier solution (M)	0.25×10^{-5}
Concentration of sodium chloride (M)	0.43
pH of carrier solution	5.2
Diameter of coil (mm)	0.8
Excitation wave length (nm)	490
Emission wave length (nm)	517

3 RESULTS AND DISCUSSION

3 • 1 Effect of Coil length and flow rate on the fluorescence intensity of fluorescein in carrier solution

Effect of coil length was studied with the injection of 0.25×10^{-5} M sodium carbonate solution. The results are shown in Figure 2. the peak height slightly decreased as the length of the reaction coil increased from 0.5 m to 2.5m. On the other hand, as shown in Figure 3, a significant decrease in peak height and a broadening of width were observed with an increasing flow rate of more than 1.5ml/min. Thus we set the flow rate at 1ml/min and the coil length at 1.5 ml/min.

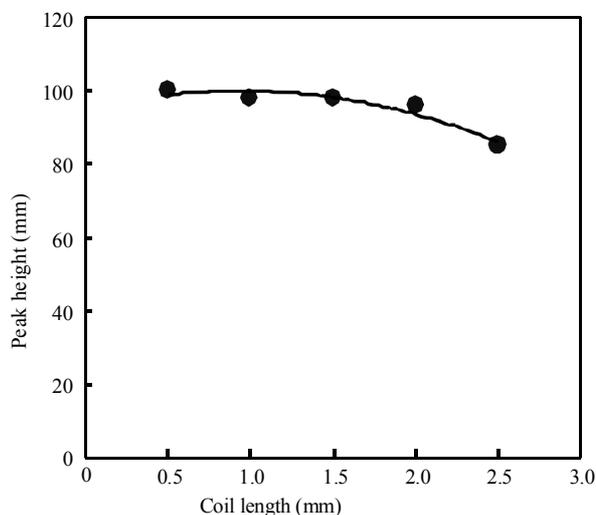


Fig.2 Effect of coil length

Fluorescein concentration: 0.25×10^{-5} M
pH:5.3, $\text{HCO}_3^-:10^{-3}$ M, Injection volume:5 μ l

3 • 2 Effect of pH on the fluorescence intensity of fluorescein in carrier solution

In order to identify the effect of pH on the fluorescence intensity of fluorescein in the carrier solution, the following experiment was performed. The initial pH value of the carrier solution was maintained at 4, and that of the carrier solution in a reservoir was adjusted by dropping diluted hydrochloric acid solution ranging from pH 4 to 8.5 stepwise. The fluorescence intensity was measured at each pH by using the FIA system described in Figure 1. The results are illustrated in Figure 4. The increase of pH, the cause of the

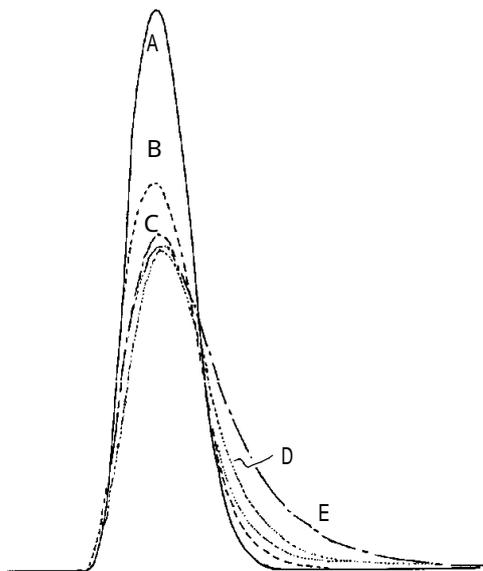


Fig.3 Effect of flow rate on the peak width of flow signals
 A:0.5 ~ 1.5 B:2.0 C:2.5 D:3.0 E:3.5
 Units:ml/min

change of fluorescence intensity due to the dissociation of fluorescein (which acts as a proton donor), caused a change of fluorescence intensity.

We applied this phenomena to the determination for alkalinity.

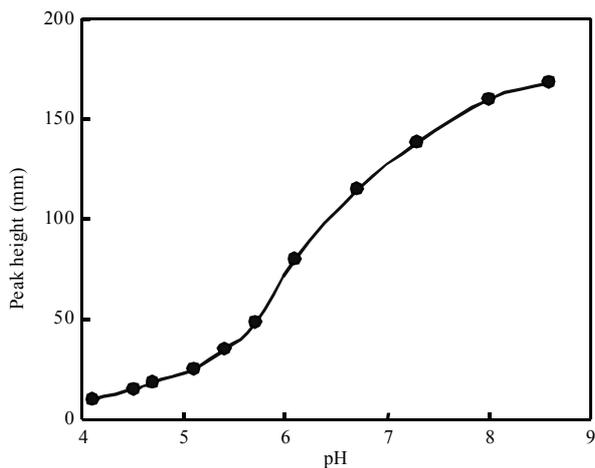


Fig.4 Effect of pH on the fluorescence intensity of fluorescein
 Fluorescein concentration: 0.125×10^{-5} M
 HCO_3^- : 10^{-3} M, Injection volume: $5 \mu\text{l}$

3 • 3 Effect of initial pH of the carrier solution on the fluorescence intensity of fluorescein

The effect of initial pH of the carrier solution on the fluorescence intensity were studied by means of injecting 0.25×10^{-5} M sodium carbonate solution. As shown in Figure 5, the peak height increased with an increase of pH in the range of 3.8 to 4.8. Maximum and constant peak heights were obtained in the pH range from 4.8 to 5.5.

On the other hand the peak broadened and tailed with the increase of pH. It was presumed that the increment of pH causes the decrease of the reaction rate between the carrier solution and carbonate ions. The most suitable pH of the carrier solution was 5.2 which was chosen for all experiments regarding the determination of alkalinity.

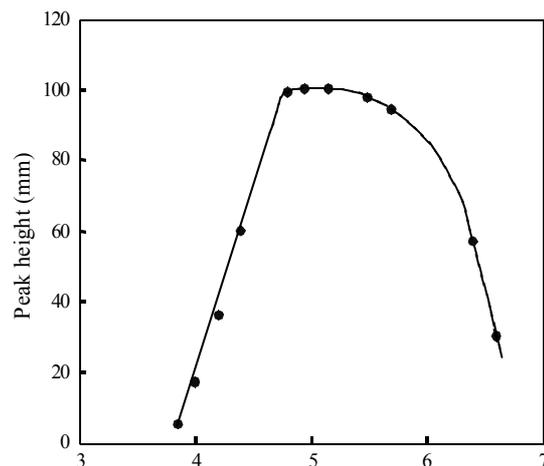


Fig.5 Effect of pH of carrier solution on the determination of alkalinity
 Fluorescein concentration: 0.25×10^{-5} M
 HCO_3^- : 10^{-3} M, Injection volume: $5 \mu\text{l}$, coil length:1.5m

3 • 4 Effect of diverse ions on the determination of alkalinity

The effects of diverse ions on the determination of 50 mg/l of CaCO_3 alkalinity were studied. The experimental results are shown in Table 2. Most cations and anions in the presence of 0.005M to 0.34M did not interfere with the

determination of alkalinity.

3 • 5 Calibration curve and precision

Figure 6 shows typical traces obtained by repeated injections of standard alkalinity solutions. A linear relationship was observed between the peak height and alkalinity concentration in the range from 0.5 to 120mg/l of CaCO₃. The detection limit was calculated from flow trace

Table 2 Tolerable amounts of divers ions on the determination of alkalinity

Ions	Added as	Tolerable amounts (M)
Na ⁺	NaCl	0.34
K ⁺	KCl	0.090
Ca ²⁺	CaCl ₂	0.0050
Mg ²⁺	MgSO ₄	0.050
NH ₄ ⁺	NH ₄ Cl	0.0090
Cl ⁻	NaCl	0.34
Br ⁻	NaBr	0.10
I ⁻	NaI	0.080
SO ₄ ²⁻	Na ₂ SO ₄	0.067
NO ₃ ⁻	NaNO ₃	0.094
NO ₂ ⁻	NaNO ₂	0.087

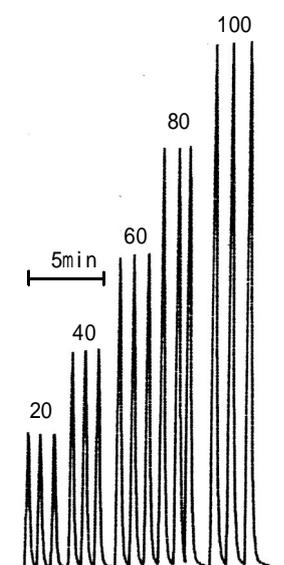


Fig.6 Typical continuous signal traces for alkalinity
Sample size:5 μ l
Concentration:20-100mg/ml as CaCO₃

(signal to noise ratio of 3).

The sampling rate was around 80 samples per hour. Turner et.al.¹¹⁾ reported that the analytical throughput was 30 samples per hour using flow injection method with

spectrophotometric titration, and was 10 to 30 minutes for conventional method (titration method). We achieved high throughput for the analysis for alkalinity compared with the conventional method. The relative standard deviation for ten determinations was 4.5% for 40 mg/l of CaCO₃ alkalinity.

3 • 6 Comparison between proposed and titration method

The validity of the proposed method has been examined by analyzing synthetic samples and real samples which were obtained from Fukuoka prefecture. The results of the proposed method were compared with those of the titration method.

The results are listed in Table 3. Based on five measurements for each sample using the respective method, the standard deviation was within 5%.

The values determined by the proposed method agreed well with those obtained by the titration method.

Table 3 Determination of alkalinity in synthetic samples and natural waters

Samples	Proposed method (mg/l)	Titration method (mg/l)
Synthetic samples 1	28.9	29.5
Synthetic samples 2	22.3	22.5
River water 1	57.8	56.0
River water 2	40.3	39.5
Tap water	22.8	24.0

4 CONCLUSIONS

The determination of alkalinity in water samples was achieved by means of the flow injection method employing a fluorescence detector. This method was based on the acid-base reaction between alkalinity and fluorescein (which was an acid). Fivemicro-liters of the sample solution were injected, and an increase in the fluorescence intensity of the fluorescein at 517 nm was detected. The dominant natural water ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ did not

interfere with the determination of alkalinity. The results of the analysis of various water samples obtained using the proposed FIA system corresponded closely to those by obtained by obtained using the standard titration method. The proposed FIA system can provide a rapid and simple analysis, with a high throughput of 80 samples per hour, requiring no complicated operation.

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アルカリ度のフローインジェクション分析

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フローインジェクション法による天然水中のアルカリ度の簡易迅速な分析法を検討した。本法はフルオレスセインの蛍光強度のpH依存性を利用したもので、その強度はアルカリ度濃度と比例する。70-系はリザーバー、ポンプ、ラインサンプラー、コイル及び蛍光検出器より構成され、5 μlの試料を70-系に注入し、フルオレスセインの蛍光強度の変化を測定する。蛍光検出器の励起及び蛍光波長はそれぞれ、490nm及び517nmである。検出限界値は CaCO₃ 換算で0.5 mg/l、変動係数は4.5%であった。分析速度は1時間当たり80試料で操作は簡便である。天然水中に存在する Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, 及び SO₄²⁻等のイオンはアルカリ度の測定に影響しない。本法の結果は滴定法の結果とよく一致した。