March, 1992] © *1992 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***65***, *911—913 (1992)* 911

Determination of Fluoride Ion by a Flow Injection Analysis Based on the Formation of a Fluorescent Aluminium-Schiff Base Complex

Izuo Aoki,* Masahiko Tuyuki, and Kunihiro Watanabe
Faculty of Science and Technology, Science University of Tokyo,
2641, Yamazaki, Noda, Chiba 278

(Received August 9, 1991)

Synopsis. In the presence of fluoride ions, aluminium reacts with *N*-salicylideneethylenediamine to form fluorescent Schiff base complexes. A flow-injection analysis system based on this reaction has been developed for a determination of the fluoride ions at the ppm level. By measuring the fluorescence intensities, the number of fluoride ions could be selectively determined over the range 0.15—10 ppm; 40 samples could be analyzed per hour. The proposed system was applied to an analysis of the fluoride ion in river water.

In the analytical field the formation of fluorescent complexes by reactions between metal ions and Schiff bases are mainly used for the determination of metal ions.[1] Although *N*-salicylideneethylenediamine (SED) reacts with beryllium,[2] magnesium,[3] and zinc[4] to form stable fluorescent complexes, no reaction takes place with aluminium. In the present study it was found that the addition of fluoride ions to a mixture of SED and aluminium resulted in the formation of a fluorescent aluminium–SED complex. Since fluoride usually acts as a quencher for fluorescent complexes, most of fluorometric methods for the determination of fluoride involve a 'quenching analysis'.[5–7] In the present paper, a flow injection analysis (FIA) of the fluoride ion based on the formaton of an aluminium–SED complex, which shows a positive response to the concentration of the fluoride ion, was investigated.

Experimental

Reagents. Standard solution of fluoride ion: A stock solution of fluoride ions (1000 ppm, 1 ppm=1 μg cm^{-3}) was prepared by dissolving 2.210 g of sodium fluoride in 1 dm^3 of distilled water. The working solution was prepared by suitable dilution with distilled water from the stock solution, and stored in a polyethylene bottle. Aluminium solution (Reagent A): 0.4744 g of aluminium potassium sulfate 24 hydrate was dissolved in 100 cm^3 of 0.18 M (1 M=1 mol dm^{-3}) sulfuric acid, and 2.5 cm^3 of the stock soltion was diluted with 100 cm^3 of 0.074 M sulfuric acid. SED solution (Reagent B): 2.011 g of *N,N'*-disalicylideneethylenediamine (DSED)[8] was dissolved in 100 cm^3 of 1,4-dioxane. On the other hand, 25 cm^3 of ethylenediamine (en) was diluted to 100 cm^3 with distilled water. To a 100 cm^3 volumetric flask, 1 cm^3 of the DSED solution, 2 cm^3 of the en solution and 20 cm^3 of 1,4-dioxane were added. The solution was diluted to 100 cm^3 with distilled water; the resultant solution was used as Reagent B.

Equipments and Procedure. Schematic diagrams of the flow-injection systems are shown in Fig. 1 Stainless-steel tubing (SUS 316, i.d. 0.5 mm) was used.[13] The carrier (distilled water) and reagent solutions were pumped at 0.5 cm^3 min^{-1} using a double-plunger pump (Nippon Seimitu Kagaku SP-D-3201). Then, 90 μdm^3 of a sample solution was injected manually into the carrier stream, after which the carrier was mixed with reagent solutions at a mixing joint. After developing a fluorescent aluminium-Schiff base complex in a reaction tube, the fluorescence intensity was measured by spectrofluorometer (Shimadzu RF-500LC, 150 W xenon lamp) equipped with a 16 μdm^3 flow-through cell. The concentration of fluoride ions was obtained from the fluorescence peak height on a recorder. The excitation and emission wavelengths were 360 and 460 nm, respectively. The sensitivity of the spectrofluorometer was calibrated by using 2 μg cm^{-3} quinine sulfate before measuring the samples.

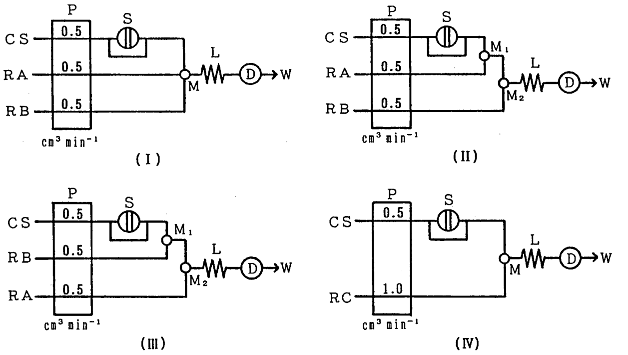


Fig. 1. Schematic diagrams of FIA systems. CS: carrier solution (distilled water), RA: Reagent A, RB: Reagent B, RC: mixture of Reagent A and Reagent B, P: pump, S: sample injector (90 μdm^3), M: mixing joint, Length between M_1 and M_2: 25 cm, L: reaction coil (0.5 mm i.d.), D: detector (λ_{ex}; 360 nm, λ_{em}; 460 nm), W: waste.

Results and Discussion

Formation of an Aluminium-Schiff Base Complex. The proposed method for the determination of fluoride ions is based on fluorescence enhancement by the presence of fluoride ions. In Reagent B, DSED reacts with the excess of en to form SED,[2] and SED reacts with aluminium ions in the presence of fluoride ions to form fluorescent complexes. This complex formation may be ascribed to a suppression of the hydrolysis of aluminium ions by fluoride ions. The excitation and emission spectra of the complex obtained were similar to those of beryllium- and magnesium-SED complexes.[2,3]

The stability of the fluorescence intensity of the aluminium complex was examined according to a batchwise procedure.[2] As shown in Fig. 2, the fluorescence intensity of the complex decreased by half within a few minutes. The absorption spectrum of the aluminium complex initially showed its maximum at

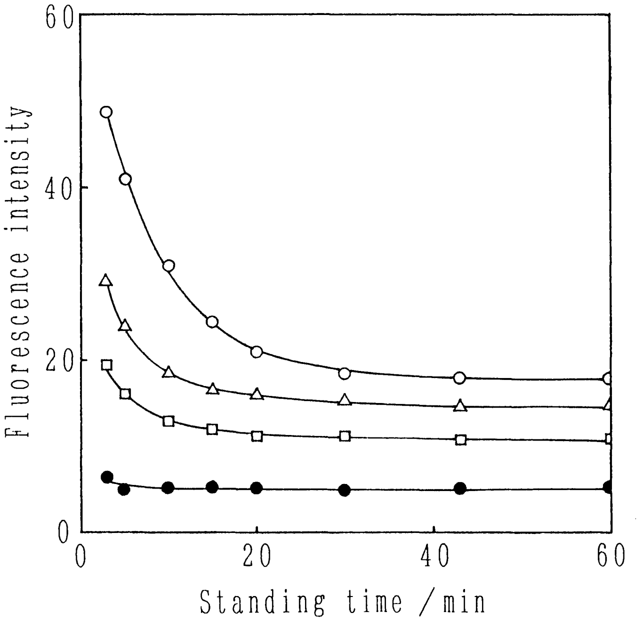
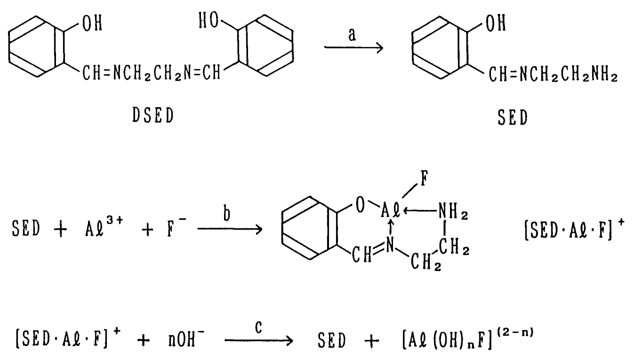


Fig. 2. Fluorescence stability measured according to a batchwise procedure. [aluminium]: 1.5×10^{-5} M, [en]: 3.0×10^{-2} M, [DSED]: 2.0×10^{-4} M, Solvent: water/1,4-dioxane=70/30 (vol/vol), pH 7.5, Wavelength: 360 nm/460 nm, [fluoride]: ○ 0.6 ppm; △ 0.4 ppm; □ 0.2 ppm; ● 0 ppm.



a) large excess of en in alkaline solution, b) neutral pH region, c) within a few minutes.

Scheme 1.

360 nm, while after 15 minutes it was almost consistent with that of the free ligand (SED).[9] It was, therefore, concluded that the complex was hydrolyzed and liberated SED. These reactions are summarized in Scheme 1.

Although the aluminium–SED complex is not stable, this reaction is useful for detecting the ppm level of the fluoride ions when the fluorescence intensity is measured as rapidly as possible. With these aspects in mind, a continuous-flow method was used in order to obtain the fluorescence intensity of the complex with sufficient reproducibility.

Development of FIA System of Fluoride Ion. In order to determine the most suitable flow system, four kinds of systems (Fig. 1) were examined regarding sensitivity. As a result of research, II and III in Fig. 1 showed an equivalent fluorescence peak height to I, while IV gave no peak, because SED hydrolyzed before mixing with the fluoride ions. System I was used in further investigations.

As can be anticipated from Fig. 2, the peak height was remarkably affected by the length of the reaction tube. A tube length of 17 cm gave the highest peak. In this case, it took 6 seconds for the sample stream to reach the detector after passing the mixing joint.

The effect of the pH on the fluorescence peak height was examined. The pH of the solution was adjusted by varing the sulfuric acid concentration in Reagent A; the pH was measured in waste. Constant heights were obtained in the pH range of 4—7. In the acidic region below pH 2, SED hydrolyzed so rapidly that the aluminium complex did not form; in the alkaline region, however, the decrease of the peak height with increasing pH could probably be ascribed to a progressive hydrolysis of aluminium ions. pH 6 was used in this FIA system.

When aliphatic monoamines, such as ethylamine and butylamine, were used instead of en in Reagent B, no fluorescence peak was observed over pH ranges 1—13. In the case of using *o*-aminophenol-related compounds[10] and amino acids,[11] fluorescent Schiff base complexes were formed, even if fluoride ions were absent. 1,2-Propanediamine and diethylenetriamine gave almost the same fluorescence intensity as en, but 1,3-propanediamine gave weak fluorescence in comparison with en.

The effects of the concentrations of aluminium, en and DSED on the fluorescence peak height were investigated, and the following conditions were selected for the FIA of fluoride ions: aluminium=2.5×10^{-4} M in Reagent A, en=7.4×10^{-2} M in Reagent B and DSED=7.5×10^{-4} M in Reagent B. In the case of DSED, although 3×10^{-3} M in Reagent B gave the maximum peak height, the signal/noise ratio decreased with increasing DSED concentration; 7.5×10^{-4} M of DSED in Reagent B gave the maximum signal/noise ratio.

Calibration Curve, and Effect of Foreign Ions. By using FIA system I, fluoride ions could be determined over the range 0.15—10 ppm within a relative standard deviation (r.s.d.) of 3%. A typical flow signal for the calibration graphs of fluoride is shown in Figure 3. The lower detection limit (signal/noise=3) of fluoride ions was 0.05 ppm. With a flow rate 0.5 $\mathrm{cm^3\,min^{-1}}$, 40 samples can be analyzed per hour.

The effects of foreign ions on the determination of fluoride ions (2 ppm) are summarized in Table 1. Among the anions examined, although oxalate, tartrate and phosphate caused relatively large errors, the others did not show any serious interference. For alkali and alkaline-earth metal ions, no serious interference was observed. The recovery test of fluoride (0.50 ppm) added to synthetic tap water was satisfactory (fluoride found : 0.49 ppm, r.s.d. : 2.9%, n=5).[14]

Determination of Fluoride Ion in River Water. The present method for the determination of fluoride ions

Table 1. Effect of Foreign Ions on the Determination of Fluoride Ion (2.0 ppm)

Ions	Ion added/ppm	Added as	Fluoride found/ppm
Chloride	1000	NaCl	2.0
Bromide	1000	NaBr	2.0
Iodide	100	KI	2.0
Carbonate	50	Na_2CO_3	2.2
Acetate	100	CH_3COONa	2.1
Nitrate	20000	KNO_3	2.0
Oxalate	100	$(COONa)_2$	5.0
Tartrate	10	$(CH(OH)COONa)_2$	2.8
Thiocyanate	10000	KSCN	2.0
Perchlorate	20000	$NaClO_4$	2.0
Nitrite	100	$NaNO_2$	1.9
Sulfite	100	Na_2SO_3	1.8
Phosphate	10	Na_3PO_4	0.6
Ammonium	100	NH_4Cl	2.0
Alminium(III)	10	$K_2Al_2(SO_4)_4 \cdot 24H_2O$	3.0
Barium(II)	100	$BaCl_2$	1.5
Cobalt(II)	50	$CoCl_2$	0.9
Cupper(II)	50	$CuCl_2$	1.3
Strontium(II)	100	$Sr(NO_3)_2$	2.0
Iron(II)	10	$Fe(SO_4)(NH_4)_2SO_4 \cdot 6H_2O$	1.1
Iron(III)	10	$Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$	1.1

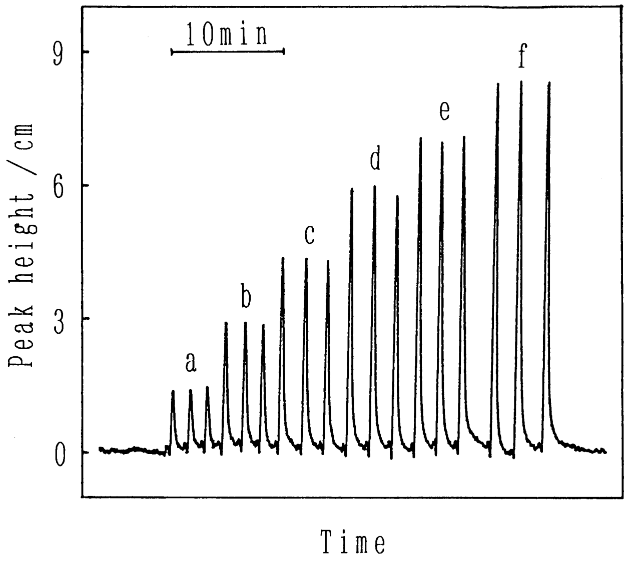


Fig. 3. Typical flow signals for calibration graphs. [fluoride]: (a) 0.5, (b) 1.0, (c) 1.5, (d) 2.0, (e) 2.5, (f) 3.0 ppm; [aluminium]: 2.5×10^{-4} M in Reagent A; [en]: 7.4×10^{-2} M in Reagent B; [DSED]: 7.5×10^{-4} M in Reagent B.

was applied to the determination of fluoride in river water (Tone-unga river, Nagareyama, Chiba). The sample solution taken was treated with a membrane filter (pore size 0.1 μm) before analysis. Good agreement was observed between the result obtained by the present method (fluoride found: 2.34 ppm) and that obtained by the lathanum-alizarin complexone method (2.29 ppm).[12]

References

1) F. D. Snell, "Photometric and Fluorometric Methods of Analysis, Metals. Part 2," John Wiley & Sons, New York (1978).

2) K. Watanabe and I. Aoki, *Bunseki Kagaku,* **34**, 497 (1985).

3) K. Watanabe and I. Aoki, *Bunseki Kagaku,* **35**, 795 (1986).

4) K. Watanabe and I. Aoki, *Bunseki Kagaku,* **35**, 1 (1986).

5) C. A. Horton, J. M. Kolthoff, and P. J. Irving, "Treatise on Analytical Chemistry, Pt. II," Interscience, New York (1961), Vol. 7, p. 268.

6) D. R. Taves, *Talanta,* **15**, 1015 (1968).

7) M. Watanabe, "Keikou Bunseki (Fluorometry)," Hirokawa (1970), p. 92.

8) D. C. Freeman, Jr. and C. E. White, *J. Am. Chem. Soc.,* **78**, 2678 (1956).

9) R. S. McQuate and D. L. Leussing, *J. Am. Chem. Soc.,* **97**, 5117 (1975).

10) I. Aoki, T. Matsunaga, and K. Watanabe, *Bull. Chem. Soc. Jpn.,* **62**, 2369 (1989).

11) K. Watanabe and I. Aoki, *Bunseki Kagaku,* **35**, 487 (1986).

12) S. Hirano, "Muki Ouyou Hishoku Bunseki 2," Kyouritu, Tokyo (1974), p. 280.

13) Teflon tubing could be used instead of stainless steel tubling.

14) Composition of synthetic tap water: calcium(II); 250, cadmium(II); 0.01, chromium(IV); 0.05, cupper(II); 1.0, iron(III); 0.30, magnesium(II); 50, lead(II); 0.10, zinc(II); 1.0, fluoride; 0.50 ppm.