Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 66 (2005) 80–85

Talanta

www.elsevier.com/locate/talanta

Automatic microdistillation flow-injection system for the spectrophotometric determination of fluoride

Katsuhisa Shimada[a,*], Tetsuro Shimoda[a], Hisao Kokusen[b], Shigenori Nakano[c,**]

[a] Aqualab Co. Ltd., Shibazaki, Tatikawa, Tokyo 190-0023, Japan
[b] Department of Environmental Chemistry, Faculty of Environmental Architecture, Kanazawa Institute of Technology, Ohgigaoka Nonoichi, Ishikawa 921-8501, Japan
[c] Department of Regional Environment, Faculty of Regional Sciences, Tottori University, Tottori 680-8551, Japan

Received 12 August 2004; received in revised form 29 September 2004; accepted 29 September 2004

Abstract

An automatic flow-injection (FI) system including on-line separation by microdistillation and spectrophotometric detection has been developed for the determination of trace amounts of fluoride. This ion was separated from sample matrix by distillation in the presence of sulfuric and phosphoric acids, and was subsequently determined with spectrophotometry based on the mixed-ligand complex of lanthanum(III)–fluoride–alizarin complexone. The proposed FI system has high sampling frequency (20 samples h^{-1}), small sample size (600 μl) and the dynamic range of 0.05–15 mg l^{-1} with relative standard deviations of below 1.2%. Interfering ions such as aluminum(III) and iron(III) was effectively eliminated. The method was successfully applied to the determination of fluoride in industrial drainage after water treatment.

Keywords: Microdistillation; Flow-injection analysis; Fluoride; Spectrophotometry; Lanthanum(III)–alizarin complexone

---

1. Introduction

Fluoride is widely distributed in natural water at low concentrations. In unpolluted fresh and sea waters, it generally exists in the range 0.01–0.3 mg l^{-1} and 1.2–1.5 mg l^{-1}, respectively [1]. Compounds of fluorine are very valuable and extensively utilized in human activities. The industrial effluent, combustion of coals and sewage discharged from the domestic water supplies contribute to an increase in fluoride levels in local aquatic systems. The health effect of fluoride such as dental fluorosis and bone fracture has been considerably attracted attention. This ion is considered to be essential to both plants and animals at low concentrations, but is toxic at high concentrations [1,2]; thus, a continuous monitoring of the presence and movement of fluoride in the environment is of importance.

The most common techniques for the fluoride determination are potentiometry with fluoride ion selective electrode (ISE) [3–7] and ion chromatography (IC) [8–10]. Although ISE methods have been widely used owing to its simplicity and short analysis time, their selectivity is rather limited. The main problem in the IC methods is the interference from monocarboxylic acids which co-eluted with or only partly resolved from fluoride [8]. Other analytical techniques for fluoride have also been reported by several authors. These include spectrophotometry [11–19], spectrofluorimetry [20–22], polarography [23,24], and capillary electrophoresis [25,26]. Spectrophotometric methods with batchwise or flow-injection (FI) procedures have been achieved high sensitivity, based on ternary fluoride complex formations such as Zr(IV)–eriochrome cyanine R [11], La(III)–alizarin complexone (La–ALC) [12,17,18], Zr(IV)–alizarin red S [13,15] and Zr(IV)–semixylenol

---

[*] Corresponding author. Fax: +81 42 521 3121.
[**] Co-corresponding author. Fax: +81 857 31 5109.
E-mail addresses: k-shimada@aqualab.co.jp (K. Shimada), nakano@fed.tottori-u.ac.jp (S. Nakano).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.09.026

orange [14]. The direct application of these methods to real samples having complex matrices is difficult because of their poor selectivity due to complex-formation of fluoride with cations such as Al(III) and Fe(III). Oszwaldowski et al. [16] developed the reversed-phase liquid chromatography with spectrophotometric detection using coloration of Zr(IV) or Hf(IV)—2-(5-brom-2-pyridylazo)-5-diethylaminophenol; trace amounts of fluoride in the range 1–150 μg l^{-1} were determined by this method. Nonchromatographic separation techniques have been used for fluoride. This ion in plant samples was separated by batch distillation in the presence of sulfuric acid and hydrogen peroxide, and was then determined with manual spectrophotometric method [18]. Gas permeable membranes were employed for the separation of fluoride [3,15]. In these methods, fluoride was converted to a volatile derivative such as trimethylfluorosilane.

Wada et al. [12] reported a FI spectrophotometric method for the determination of fluoride using the complex formation of La–ALC. The determinable range of this method was 0.03–1.2 mg l^{-1} fluoride, but Al(III), Ca(II), Fe(III) and phosphate interfered with the fluoride determination; these interfering ions should be eliminated by an appropriate separation method. Conventional distillation procedures for fluoride separation were too time-consuming; the distillation time was about 80 min per one sample. Thus, a rapid and simple method for the determination of fluoride is desirable for its routine analysis.

The present authors designed a mini-condenser for developing computer control of a distillation FI system. This paper describes an automated FI method for the determination of trace amounts of fluoride using combination of on-line separation by microdistillation and spectrophotometric detection based on its complex formation of La–ALC. The sampling frequency of the present system was 20 samples h^{-1} with the dynamic range of 0.05–15 mg l^{-1}. The reproducibility of the method is satisfactory with relative standard deviations of less than 1.2%. The system showed good selectivity to fluoride with respect to possible interfering ions such as Al(III) and Fe(III). The proposed method was successfully applied to the determination of fluoride in industrial drainage after water treatment by coagulation.

2. Experimental

2.1. Reagent

All chemicals used were of analytical reagent grade. Ultrapure water obtained from a NANOpure Dlamond (Barnsted Inc.) system was used for the preparation of all solutions.

A stock solution of fluoride (100 mg l^{-1}) was prepared by dissolving 0.111 g of sodium fluoride (Wako Junyaku Co., Japan), dried at ca. 110 °C for 4 h, in 500 ml water. The working standard solutions were prepared by appropriate dilution of the stock solution with water. The mixture of 40% (v/v) sulfuric and 1.0% (v/v) phosphoric acids was prepared as a distillation solution.

Alfusone contained 2.5% (w/w) La–ALC (mole ratio, 1:1), hexamethylenetetramine and potassium hydrogen phthalate was purchased from Dojindo Lab., Japan. A 0.7% (w/v) alfusone solution was prepared by dissolving 3.5 g of the commercial reagent in 50 ml of water and 350 ml of acetone. After that, its pH value was adjusted to 4.5 by adding 2 M acetic acid and the solution was made up to 500 ml with water.

2.2. Apparatus

Fig. 1 shows a schematic representation of the automated microdistillation FI system. The system was constructed from three parts, i.e., units of an auto sampler, a microdistillation and a detection. The Aqualab AS-100 auto sampler was contained a controller and a sampling table unit. The distillation unit consisted of the following components; two Aqualab RX-530 double-plunger micro pumps, an aluminum block for heating (175 mm length × 55 mm i.d.), a home-made water-jacketed glass condenser (distillation column, 75 mm length × 10 mm i.d.; cooling column, 75 mm length × 8 mm i.d.) with a trap of ca. 500 μl (Fig. 2), a Tokyo Rikakikai CCA-1100 refrigerator, two Iwaki APN-10GD2-W diaphragm pumps, an Aqualab VE-160L six-way valve, an Ueruko WPX-1-G2.38S4-1/8J rotary pump and a Matsushita Seiko FPG-C32T2 sequence controller. A heating coil rolled around the aluminum block was made of PFA tubing (5.0 m length × 2 mm i.d.). The detection unit consisted of an Aqualab RX-520 double-plunger micro pump, an Iwaki APN-10GD2-W diaphragm pump, a reaction coil in an Aqualab R-500 thermostated bath and a Soma Kougaku S-3250 spectrophotometer with a micro flow cell (10-mm path length, 8 μl). The flow lines except for the heating coil were made of PTFE tubing (0.5 mm i.d.) and connectors. Data acquisition and system control were achieved using a data-processing computer (Sharp Co., Japan, MEBIUS) fitted with an Aqualab DS-100 software. A Dionex Dxi-500 ion chromatographic system and a Hitachi U-2000A spectrophotometer were also used.

2.3. Procedure

Analytical conditions and program sequence in the proposed system were shown in Tables 1 and 2, respectively. As shown in Fig. 1, water as a carrier for sample solution (R1) and a mixture of 40% (v/v) sulfuric and 1.0% (v/v) phosphoric acids (R2) were pumped at a flow rate of 1.0 ml mim^{-1} in the distillation unit. A 0.7% (w/v) alfusone solution (R3) and water as a carrier for a distillated solution (R4) were propelled at a rate of 0.4 ml min^{-1} in the detection unit. Following procedures were automatically performed by the control of computer. An aliquot of sample solution (600 μl) was injected into the carrier solution by the auto sampler at 3-min intervals. It was merged with the mixture of sulfuric and

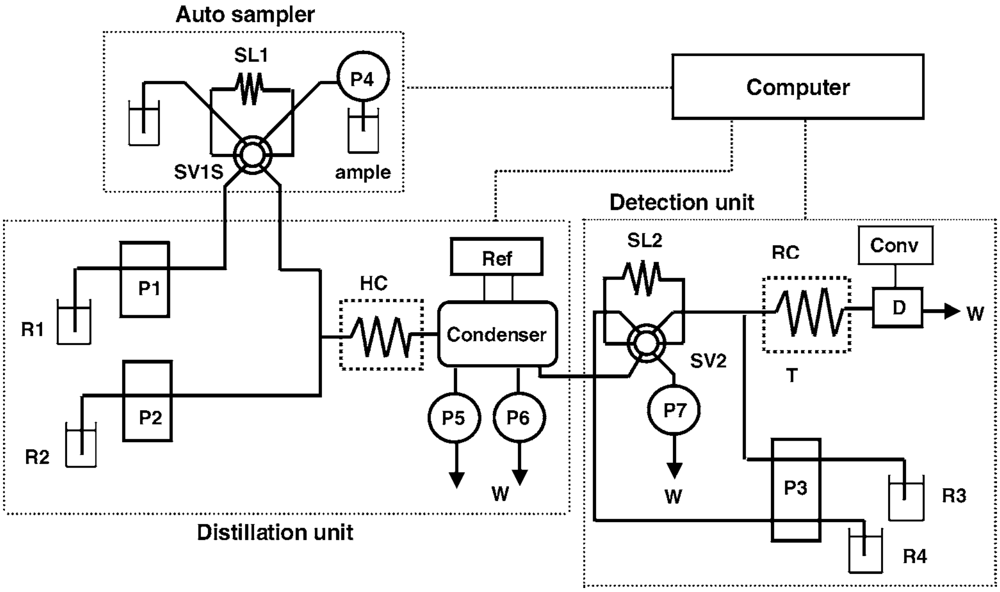

Fig. 1. Schematic diagram of the automated microdistillation flow-injection system. P1–P7, pump; R1–R4, reservoir; SV1, SV2, six-way valve; SL1, SL2, sample loop for distillation and detection, respectively; HC, heating coil; Ref, refrigerator; RC, reaction coil; T, thermostated bath; D, detector; Conv, converter; W, waste.

phosphoric acids and propelled to the heating coil (160 °C). And then it was passed through a condenser and collected in a trap, in which a 400 μl of distilled solution was subsequently introduced into the detection line at a flow rate of 1.3 ml min^{-1}. It was then mixed with the alfusone solution and was pumped to the reaction coil in the thermostated bath at 50 °C. The colored solution passed through the flow-cell. The change in the absorbance at 620 nm was measured with the spectrophotometer. The absorbance was converted to mV

Table 1
Operating conditions for the separation and detection of fluoride

Distillation	
Sample volume for distillation (μl)	600
Reservoir	
R1	Water
R2	40% (v/v) Sulfuric and 1% (v/v) phosphoric acids
Flow rate (ml min^{-1})	
P1	1.0
P2	1.0
P4	3.0
P5	1.3
P6	0.1
Heating coil length (m)	5 (2 mm i.d.)
Heating coil temperature (°C)	160
Trap (μl)	500
Detection	
Reservoir	
R3	0.7% (w/v) Alfusone in 70% (v/v) acetone (pH 4.5)
R4	Water
Flow rate (ml min^{-1})	
P3	0.4
P7	1.3
Sample volume for detection (μl)	400
Reaction coil length (m)	3 (0.5 mm i.d.)
Reaction temperature (°C)	50
Wavelength (nm)	620

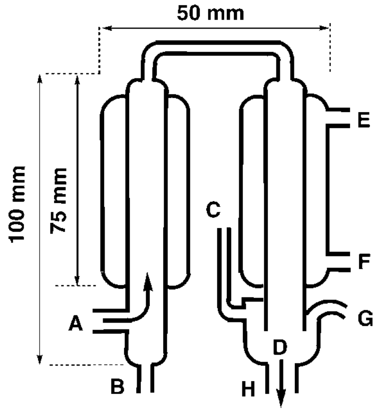

Fig. 2. Cross-section of the mini-condenser. A, inlet for water vapor; B, outlet for water drop; C, outlet for air; D, trap; E, inlet for cooling water; F, outlet for cooling water; G, outlet for overflow; H, outlet for distillated solution.

Table 2
Microdistillation and detection program sequence

Stage	Operation	Time (s)
1	Line washing (auto sampler)	60
2	Sample loading for distillation (SL1)	12
3	Changing SV1-valve position (injection for distillation)	1
4	Distillation	75
5	Sample loading for detection (SL2)	60
6	Changing SV2-valve position (injection for detection)	1
7	Detection	300

unit (1 mV = 0.001 absorbance) by the converter and the signal was sent to the data-processing computer.

3. Results and discussion

3.1. Optimization of the distillation system

In order to ensure the accuracy and precision of the fluoride determination, the inflow and outflow rates of distilled water should be balanced in a trap. To overcome this problem, a mini-condenser shown in Fig. 2 was designed and tested in the preliminary experiments. For controlling the internal pressure of the trap, droplets of water which stopped up the outlets owing to their surface tension were removed from the outlets B and G by the two pumps at a rate of 1.3 (P5) and 0.1 ml min^{-1} (P6), respectively. The water vapor flowed into the condenser through the inlet A and the distilled water flowed out it through the outlet H. This devise could realize the constant mass transport in the system.

By using the distillation system as shown in Fig. 1, three types of tubing (2 mm i.d.) made from poly ether ether ketone (PEEK), poly tetra fluoro ethylene (PTFE) and tetra fluoroethylene perfluoroalkoxy vinyl ether copolymer (PFA) were tested as a heating coil. Table 3 shows the recovery (ratio between experimental and calculated volumes) of the distilled water in the trap by using PEEK, PTFE and PFA with their different coil lengths. As can be seen, a maximum recovery for each tubing was obtained at 5 m because of balancing between the volumes of water vapor generated and the cooling capacity of the condenser. Of these, the recovery using the PEEK tubing was the highest; it was considered that the steam was scarcely leaked from the inside of the tubing toward outside. However, the durability of this tubing was poor in the sulfuric and phosphoric acids at high temperatures. Although the recovery for PFA tubing was inferior to that for the PEEK tubing, a 5-m length of PFA tubing was selected as a heating coil owing to its good durability.

Fig. 3 shows the effect of total flow rate of pumps 1 and 2 on the recovery of distilled water at different temperatures. The recovery increased with increasing in flow rate up to 2.0 ml min^{-1} and temperature up to 160 °C. And then it decreased at above this flow rate and temperature, because the mini-condenser was not capable of cooling a large amount of the water vapor. The total flow rate was thus fixed at 2.0 ml min^{-1} and a heating temperature of 160 °C was selected for the distillation step.

Table 3
Recovery of water in the trap after distillation

Coil length (m)	Recovery (%)		
	PEEK	PTFE	PFA
3	35.6	24.6	31.6
5	53.5	35.3	51.1
10	46.2	27.9	42.7

PEEK, poly ether ether ketone; PTFE, poly tetra fluoro ethylene; PFA, tetra fluoroethylene perfluoroalkoxy vinyl ether copolymer. Conditions as in Table 1 (distillation unit) except for tubing length.

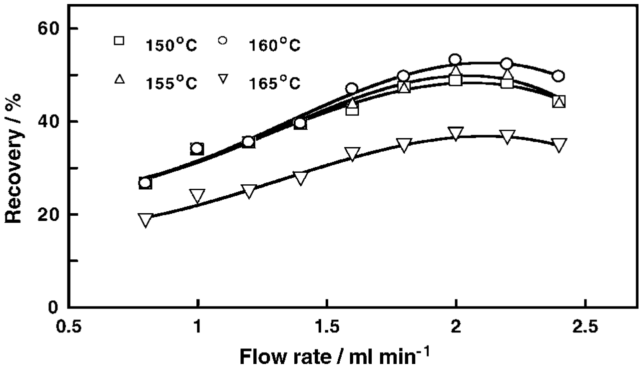

Fig. 3. Effect of flow rate and heating temperature on the recovery of water in the trap after distillation. Conditions as in Table 1 (distillation) except for flow rate and heating temperature.

In batch distillation procedures, perchloric or sulfuric acids have been used as a distillation acid for converting fluoride ion into hydrogen fluoride. Furthermore, the addition of phosphoric acid to the acidic solution was recommended because of the prevention from the interferences [11]. Fig. 4 shows the effect of the concentration of sulfuric or perchloric acids containing 1% (v/v) phosphoric acid on the determination of 10 mg l^{-1} fluoride. The peak height for fluoride in the presence of sulfuric acid was higher than that in the presence of perchloric acid. The peak height increased with increasing the acid concentrations up to 40% (v/v), and then decreased at higher concentrations. Therefore, sulfuric acid was chosen as a distillation acid and its concentration was fixed at 40% (v/v) for the distillation system.

The effect of the sample volume for distillation was examined by injection of 10 mg l^{-1} fluoride solution. The volume had a marked influence on the peak height as it increased with increasing the volume. A 600 μl of volume was selected as a compromise between sensitivity and sampling frequency.

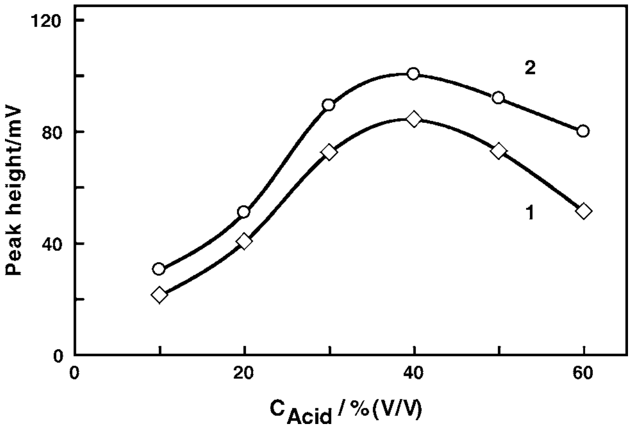

Fig. 4. Effect of the concentration of sulfuric or perchloric acid on the peak height. C_{F^-}, 10 mg l^{-1}. Conditions as in Table 1 except for the sulfuric acid concentration.

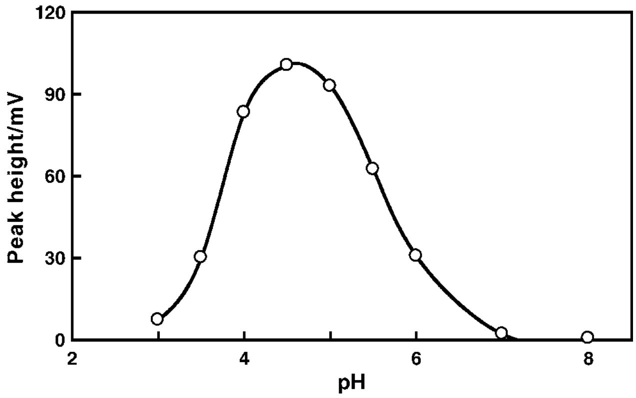

Fig. 5. Effect of pH on the peak height. C_{F^-}, 10 mg l^{-1}. Conditions as in Table 1 except for the reaction pH.

3.2. Effect of reaction variables

The reaction variables such as flow rate, pH, reaction temperature, reaction coil length and reagent concentrations were optimized by using a standard fluoride solution (10 mg l^{-1}) under the on-line distillation conditions described above.

The flow rates of both alfusone and water streams were simultaneously changed in the range 0.2–1.0 ml min^{-1}. The peak heights for fluoride were almost constant in this range; these solutions were propelled at a flow rate of 0.4 ml min^{-1} by considering the reagent consumption. Fig. 5 shows the effect of pH on the peak height by changing the amount of acetate buffer in the alfuson solution. A maximum peak height was obtained at around pH 4.5, which was somewhat distinct from that reported by Wada et al. [12] due to the difference of reaction conditions. The complex formation was thus carried out at pH 4.5. The peak height increased with increasing in reaction temperature up to 50 °C and then decreased at above this temperature; the reaction was carried out at 50 °C. The effect of reaction coil length on the peak height was examined in the range 1–10 m; a highest peak height was obtained at a coil length of 3 m. This reaction coil was adopted for the present system. The effect of distilled sample volume sent to the analytical line was examined in the range 200–600 μl. The highest peak height was obtained at 400 μl; this volume was selected in the system. An increase in the alfuson concentration increased the peak height. A constant peak height was obtained at concentrations above 0.6% (w/v). Thus, the concentration of alfusone solution was fixed at 0.7% (w/v). An increase in the acetone concentration also increased the peak height, and then it decreased at concentrations above 70% (v/v); this concentration was used for the procedure.

3.3. Calibration curve

The calibration curves were constructed under the optimized conditions described above. The peak heights were directly proportional to the concentration of fluoride in the range of 0.05–15 mg l^{-1} with the linear regression equation of $H_p = 4.82\,C_{F^-} + 3.09$ ($R^2 = 0.9946$), where H_p is peak height in mV and C_{F^-} is the fluoride concentration in mg l^{-1}. The detection limit as three times the standard deviation of the blank was 0.01 mg l^{-1}. The reproducibility was satisfactory with relative standard deviations of 1.2, 1.0, 0.5, 0.3 and 0.2% in 10 determinations of 0.5, 1.0, 5.0, 10 and 15 mg l^{-1} fluoride, respectively. The rate of sample throughput was 20 samples h^{-1}.

3.4. Effect of diverse ions

The effect of diverse ions was examined in the determination of 7.5 mg l^{-1} fluoride. The tolerable concentration was defined as the amount of added ion causing below 5% error. The results are summarized in Table 4. In the FI method using the complex formation of La-ALC without separation, tolerance levels of Al(III), Ca(II) and Fe(III) were 0.05, 1.6 and 1.2 mg l^{-1}, respectively [12]. The selectivity of the present system was greatly improved in comparison with that without distillation step; especially 100 mg l^{-1} of Al(III) and 200 mg l^{-1} of Fe(III) did not interfered with the determination of fluoride.

3.5. Application

The proposed method was applied to the determination of fluoride in industrial drainage after treatment with coagulation in order to evaluate its accuracy and applicability to real samples. The drainage samples were filtered through 0.45 μm

Table 4
Effect of diverse ions in the determination of 7.5 mg l^{-1} fluoride

Ion added	Amount added (mg l^{-1})	F^- found (mg l^{-1})	Ion added	Amount added (mg l^{-1})	F^- found (mg l^{-1})
Al(III)	500	4.5	Mn(II)	500	7.7
	200	7.5	Zn(II)	250	7.5
Ca(II)	500	7.6	NH_4(I)	200	7.4
Cu(II)	500	7.7	Cl^-	800	7.5
Fe(II)	120	1.9	NO_2^-	500	7.6
	50	7.5	NO_3^-	500	7.6
Fe(III)	150	6.5	PO_4^{3-}	500	7.7
	100	7.6	SO_4^{2-}	3000	7.5
Mg(II)	450	7.5	SiO_3^{2-}	450	7.6

Table 5
Determination of fluoride in the industrial drainage

Sample number	Fluoride found[a] ($mg\,l^{-1}$)		
	Proposed method	IC[b]	SP[c]
1	4.5 ± 0.1	4.5 ± 0.1	–
2	5.4 ± 0.2	5.3 ± 0.3	–
3	7.3 ± 0.1	7.4 ± 0.1	–
4	3.2 ± 0.3	3.1 ± 0.1	–
5	6.5 ± 0.2	6.3 ± 0.1	–
6	10.6 ± 0.4	10.6 ± 0.4	–
7	1.2 ± 0.1	1.1 ± 0.1	–
8	7.3 ± 0.3	7.4 ± 0.3	–
9	13.5 ± 0.2	13.5 ± 0.2	–
10	0.89 ± 0.02	0.86 ± 0.03	0.8 ± 0.2
11	2.9 ± 0.1	2.9 ± 0.2	–
12	9.1 ± 0.1	9.1 ± 0.2	–
13	0.42 ± 0.02	0.42 ± 0.01	0.4 ± 0.1
14	0.38 ± 0.02	0.35 ± 0.01	0.3 ± 0.1
15	0.59 ± 0.02	0.54 ± 0.05	0.5 ± 0.2

[a] Average and standard deviation for three determinations.
[b] Ion chromatography.
[c] Spectrophotometry with batch distillation.

membrane filter and the determination of fluoride was carried out by the present method. Fluoride in the same samples were also analyzed by IC and spectrophotometry combined with the batch distillation [17] to validate the present method. Table 5 shows the results obtained by the present method together with those obtained by IC and spectrophotometry. The analytical values obtained by the present method are in good agreement with those obtained by IC and spectrophotometry.

4. Conclusions

This paper demonstrated that the automated FI system containing on-line microdistillation and spectrophotometric detection allowed the rapid determination of fluoride in industrial drainage after coagulation treatment. In this system, the high sampling frequency was achieved with relative standard deviations of less than 1.2%. The present system increased the tolerance levels of interfering ions such as Al(III), Ca(II) and Fe(III). The proposed method can be used for on-line fluoride monitoring of water samples.

Acknowledgements

We appreciate Dia Instruments Co., Japan and HME Co., Japan for cooperation in this work.

References

[1] J.A. Camargo, Chemosphere 50 (2003) 251.
[2] F.L. Cerklewski, Nutr. Res. 17 (1997) 907.
[3] I. Papaefstathiou, M.T. Tena, M.D. Leque de Castro, Anal. Chim. Acta 308 (1995) 246.
[4] R.W. Kahama, J.J.M. Damen, J.M. ten Cate, Analyst 122 (1997) 855.
[5] H. Hara, K. Yabuuchi, M. Higashida, M. Ogawa, Anal. Chim. Acta 364 (1998) 117.
[6] R. Perez-Olmos, M.B. Etxebarria, J.L.F.C. Lima, M.C.B.S.M. Montenegro, Fresenius J. Anal. Chem. 362 (1998) 230.
[7] A.O. Al-Othman, J.A. Sweileh, Talanta 51 (2000) 993.
[8] J. Weiss, S. Reinhard, C. Pohl, C. Saini, L. Narayaran, J. Chromatogr. A 706 (1995) 81.
[9] C.A. Lucy, J. Chromatogr. A 739 (1996) 3.
[10] P.E. Jackson, C.A. Pohl, Trends Anal. Chem. 16 (1997) 393.
[11] D.F. Boltz, Colorimetric Determination of Nonmetals, Interscience, New York, 1958.
[12] H. Wada, H. Mori, G. Nakagawa, Anal. Chim. Acta 172 (1985) 297.
[13] T.J. Cardwell, R.W. Cattrall, M. Mitri, I.C. Hamilton, Anal. Chim. Acta 214 (1988) 433.
[14] A. Yuchi, N. Hokari, H. Wada, G. Nakagawa, Analyst 118 (1993) 219.
[15] T.J. Cardwell, R.W. Cattrall, M. Mitri, Talanta 41 (1994) 115.
[16] S. Oszawaldowski, R. Lipka, T. Majewaski, M. Jarosz, Analyst 123 (1998) 1529.
[17] Japanese Industrial Standard Committee, Testing Methods for Industrial Wastewater, JIS K0102 (1998).
[18] H.B. Li, X.R. Xu, Talanta 48 (1999) 57.
[19] D.G. Themelis, P.D. Tzanavaras, H.D. Tzanavaras, J. Pharm. Biomed. Anal. 25 (2001) 971.
[20] D. Chen, M.D. Luque de Castro, M. Valcarcel, Anal. Chim. Acta 234 (1990) 345.
[21] J. Nishimoto, T. Yamada, M. Tabata, Anal. Chim. Acta 428 (2001) 201.
[22] M. Garrido, A.G. Lista, M. Palomeque, B.S. Fernandez Band, Talanta 58 (2002) 849.
[23] L. Guanghan, L. Xiaoming, H. Zhike, H. Shuanglong, Talanta 38 (1991) 977.
[24] L. Guanghan, W. Qiongling, W. Xiaogang, Z. Tong, Y. Xin, Food Chem. 66 (1999) 519.
[25] T. Wang, S.F.Y. Li, J. Chromatogr. A 781 (1997) 457.
[26] K. Fukushi, S. Takeda, K. Chayama, S. Wakida, J. Chromatogr. A 834 (1999) 349.