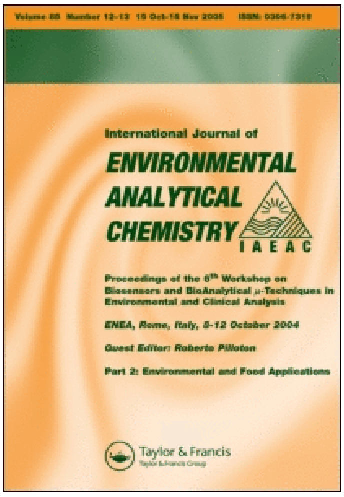

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ELIMINATION OF METAL INTERFERENCE IN THE DETERMINATION OF FLUORIDE ION BY NON-SUPPRESSOR TYPE ION CHROMATOGRAPHY

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A simple method has been developed to eliminate metal interferences in the ion-chromatographic determination of fluoride ion in aqueous solutions. Negative interferences become appreciable on 0.2-mM F^- at 0.01 to 0.02 mM of Al(III), Ce(IV), La(III), Y(III), Ce(III) and Pb(II); and at 0.25 mM of Ca(II). The interference from Cd(II), Co(II), Fe(II) and Ni(II) is insignificant at ≤ 5.0-mM metal for 5.0-mM F^-.

By alkalifying F^- solutions at pH 12.3, the metal interference can be eliminated up to the concentrations of 0.25-mM Al(III), La(III) and Y(III); 1.0-mM Ce(IV); 2.5-mM Ce(III); and 5.0-mM Pb(II), Cd(II), Co(II), Fe(II) and Ni(II). The Ca(II) interference cannot be eliminated. The pretreatment enables determination of 0.2- to 5.0-mM F^- in presence of 0.25-mM Al(III) or La(III) with coefficient-of-variations of 1.99 to 6.20%.

KEY WORDS: Ion chromatography, fluoride analysis, metal interference, alkali pretreatment.

INTRODUCTION

Analysis of anions in aqueous solutions has been conducted mainly by colorimetric methods which require tedious procedures. Recently, a rapid sequential determination of anions has become possible by ion chromatography using a column with a small ion-exchange capacity. The ion chromatography has been adopted as the official method[1-3], for the determination of anions such as fluoride, chloride, nitrate and sulfate ions. The determination of F^- ion is not free from interferences from various metal ions[4-8], since the F^- ion forms a very stable metal complex with such elements. To eliminate metal interferences, a distillation process has been proposed as the pretreatment, where F^- is separated from the metals in the form of volatile fluorosilicate[9,10]. However, the following problems have been noticed with this process: the recovery of F^- is only 64 to 75%; 3 to 4 h are required for each run; and a corrosive gas is formed from 1,1,2,2 tetrachloroethane which is used as a heat medium. It has therefore been required to

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* Corresponding author.

develop a simple and effective method to eliminate these metal interferences. In this paper, we report that in the determination of F^- ion by non-suppressor type ion chromatography the metal interferences can be reduced to a great extent only by alkalifying the F^- solutions at pH 12.3.

EXPERIMENTAL

Materials

Fluoride solutions were prepared by dissolving sodium fluoride in ultra pure water (>16 MΩ·cm). Sulfates or nitrates of Al(III), Ca(II), Cd(II), Ce(III), Ce(IV), Co(II), Fe(II), La(III), Ni(II), Pb(II) and Y(III) were dissolved also in ultra pure water and added to a F^- solution. All the chemicals were of reagent grade.

Determination of fluoride ion

Fluoride ion was determined with a non-suppressor type ion chromatograph (HIC 6A, Shimadzu Corp., Japan). It is composed of a pump, separation column, guard column, column oven, conductivity detector, degasser, auto-injector and computer. The separation column is made of stainless steel, 4.6 mm in diameter and 100 mm long, and packed with an anion exchange resin, i.e. polymethacrylate loaded with quaternary ammonium base. A mixture of 2.5-mM phthalic acid and 2.4-mM 2-amino-2-hydroxymethyl-1,3-propanediol was used as eluent (pH 4.11). The analytical conditions were as follows: detector full-scale, 0.8 μS/cm; eluent flow rate, 1.5 ml/min; column temperature, 40°C; and sample volume, 20 μl. Fluoride ion was quantified by calculating a chromatogram peak area with the attached computer.

Interference from metal ions

A 50 ml of 0.2-, 1.0- or 5.0-mM F^- solutions containing 0.01- to 25-mM Al(III), Ca(II), Cd(II), Ce(III), Ce(IV), Co(II), Fe(II), La(III), Ni(II), Pb(II) or Y(III) ion were prepared. The F^--metal solution was allowed to stand to attain equilibrium for more than one week at room temperature. An aliquot of the solution was filtered with a 0.22-μm membrane filter (Millipore GSWP025). The filtrate was analyzed for F^- ion according to the above-mentioned method.

Elimination of metal interference by alkali pretreatment

The same F^--metal solution as those used in the above experiment was vigorously shaken to homogeneously suspend metal fluoride precipitate which formed at high concentrations of F^- and metal ions. A 10 ml of the F^--metal solution was taken, to which 1.25 ml of 200-mM NaOH was added. The sample was allowed to stand overnight at room temperature to complete hydrolysis of the metal ion and then filtered. The filtrate was analyzed for F^- ion in the same way as above. Standard F^- solutions for calibration were also processed in the same way.

RESULTS AND DISCUSSION

Interference from metal ions

By adding high concentrations of Ce(III), Ce(IV), La(III), Y(III), Ca(II), Pb(II) and Fe(II) ions to F^- solutions, the formation of a white metal fluoride precipitate was observed, depending on the F^-/metal concentrations, pH and time. The precipitate was removed by filtration prior to the ion-chromatographic measurement. Conversely, no precipitate was observed when Al(III), Cd(II), Co(II) and Ni(II) ions were added.

The chromatograms of metal-free 1.0-mM F^-, 1.0-mM F^- + 0.25-mM Al(III) and 1.0-mM F^- + 1.0-mM Al(III) solutions are shown in Figures 1 A, B and C, respectively, as an example of metal interference. The peaks of sulfate ion in the chromatograms are derived from $Al_2(SO_4)_3$ which was used to prepare the Al(III) solution. The metal-free 1.0-mM F^- solution shows a very sharp peak at 1.8 min of retention time (Figure 1 A). Although there is no change in the retention time by the existence of 0.25-mM Al(III), the F^- peak is significantly reduced in its height (Figure 1 B). In presence of 1.0-mM Al(III), the F^- peak is very weak and seriously distorted and the detection of F^- ion is almost impossible (Figure 1 C). Thus, it is evident that Al(III) ion causes a serious interference in the determination of F^- ion.

The peak areas of 0.2-, 1.0- and 5.0-mM F^- ion in presence of various concentrations of Al(III), Ce(III), Ce(IV), La(III) and Y(III) ions are shown in Figures 2 to 6. The peak areas in Figures 2 to 12 are expressed in terms of percentage to those of F^- ion in absence of metal ions. It is shown that these five metal ions exhibit very serious interferences on the F^- determination. An appreciable decrease in the peaks of 0.2- and 1.0-mM F^- is found when only 0.01 to 0.02 mM of metal ions were present. For 5.0-mM F^-, appreciable interferences were found with the occurrence of 0.10- to 0.25-mM of metals. The F^- peaks decrease with increase in the interfering metal concentrations. When those metal ions are contained at higher concentrations than those of F^- ion, no peaks can be detected. The interferences from those metals are more serious on the lower concentrations of F^- ion.

The interference from Ca(II) ion becomes significant from the concentrations of 0.25 mM (Figure 7). In presence of 5.0 mM or higher concentrations of Ca(II) ion, the F^- peak can not be detected. Unlike the interference from the other metals, the Ca(II) interference is slightly more serious on higher concentrations of F^- ion. The interference from Pb(II) ion becomes appreciable from the concentrations of 0.02 mM for 0.2-mM F^-; 0.05 mM for 1.0-mM F^-; and 0.25 mM for 5.0-mM F^- (Figure 8). But the Pb(II) interference is less serious in comparison to those from Al(III), Ce(III), Ce(IV), La(III), Y(III) and Ca(II) ions. The F^- peak can be detected even in presence of equal concentration of Pb(II) ion to that of F^- ion. Interferences occur by the addition of Cd(II), Co(II), Fe(II) and Ni(II) ions but the extent seems lower (Figures 9 to 12). In presence of 5.0 mM of those metal ions, the peaks of 0.2-mM F^-, 1.0-mM F^- and 5.0-mM F^- ions correspond to more than 60, 90 and 90% of those of metal-free F^- ion, respectively. Interference from those metal ions at 5.0 mM are practically negligible for 5.0-mM F^-.

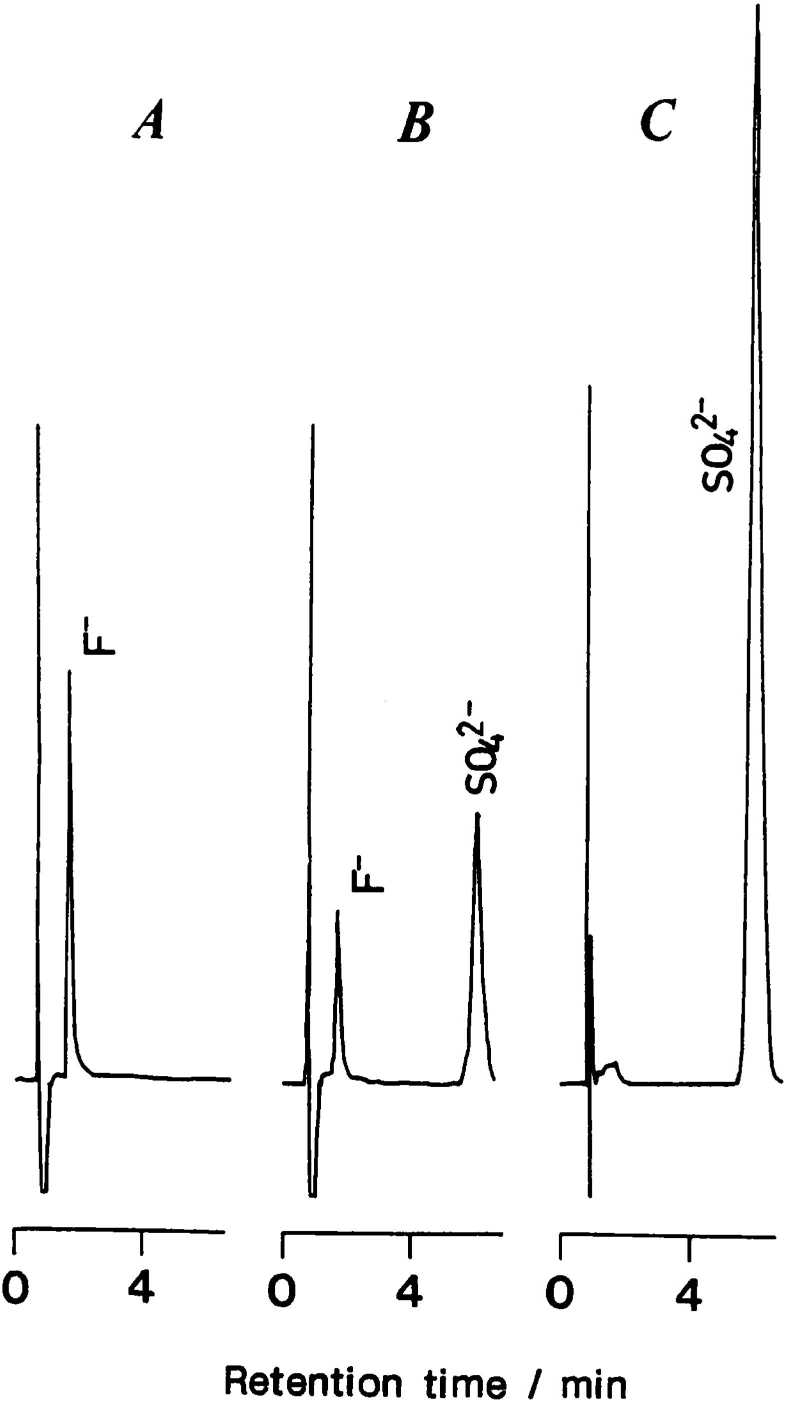

Figure 1 Chromatograms of F⁻ ion in the presence of Al(III) ion.
F⁻: 1.0 mM.
Al(III): (A), 0 mM; (B), 0.25 mM; (C), 1.0 mM.

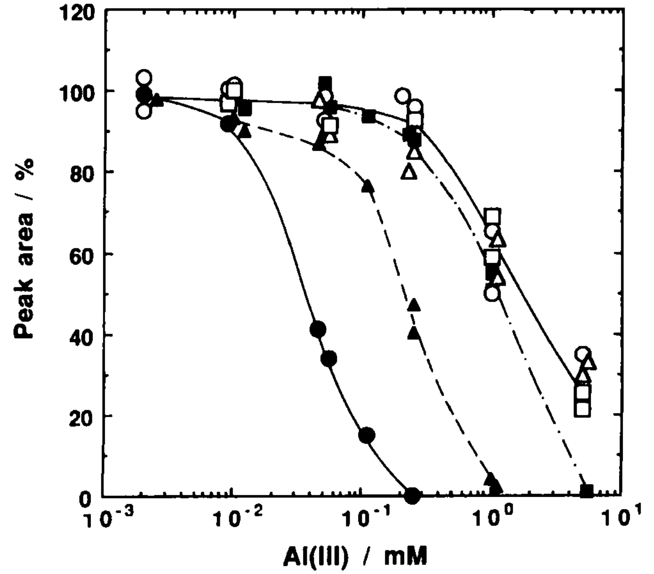

Figure 2 Interference from Al(III) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F^- ion.
Without pretreatment: ●, 0.2 mM F^-; ▲, 1.0 mM F^-; ■, 5.0 mM F^-.
With pretreatment: ○, 0.2 mM F^-; △, 1.0 mM F^-; □, 5.0 mM F^-.

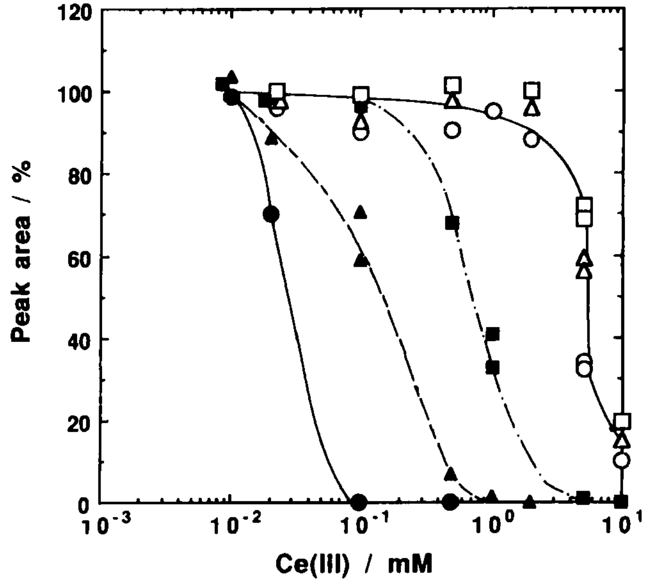

Figure 3 Interference from Ce(III) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F^- ion.
Without pretreatment: ●, 0.2 mM F^-; ▲, 1.0 mM F^-; ■, 5.0 mM F^-.
With pretreatment: ○, 0.2 mM F^-; △, 1.0 mM F^-; □, 5.0 mM F^-.

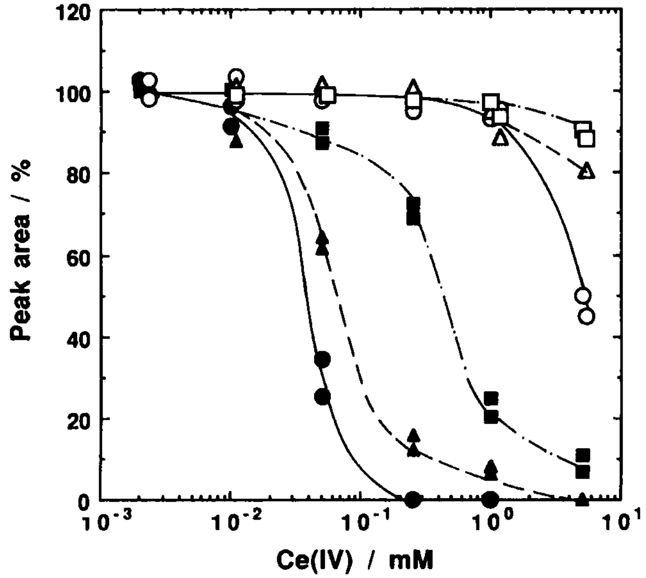

Figure 4 Interference from Ce(IV) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F⁻ ion.
Without pretreatment: ●, 0.2 mM F⁻; ▲, 1.0 mM F⁻; ■, 5.0 mM F⁻.
With pretreatment: ○, 0.2 mM F⁻; △, 1.0 mM F⁻; □, 5.0 mM F⁻.

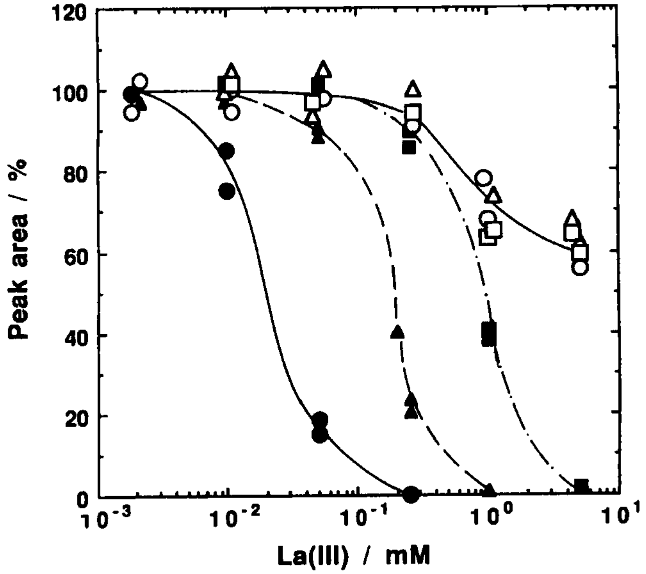

Figure 5 Interference from La(III) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F⁻ ion.
Without pretreatment: ●, 0.2 mM F⁻; ▲, 1.0 mM F⁻; ■, 5.0 mM F⁻.
With pretreatment: ○, 0.2 mM F⁻; △, 1.0 mM F⁻; □, 5.0 mM F⁻.

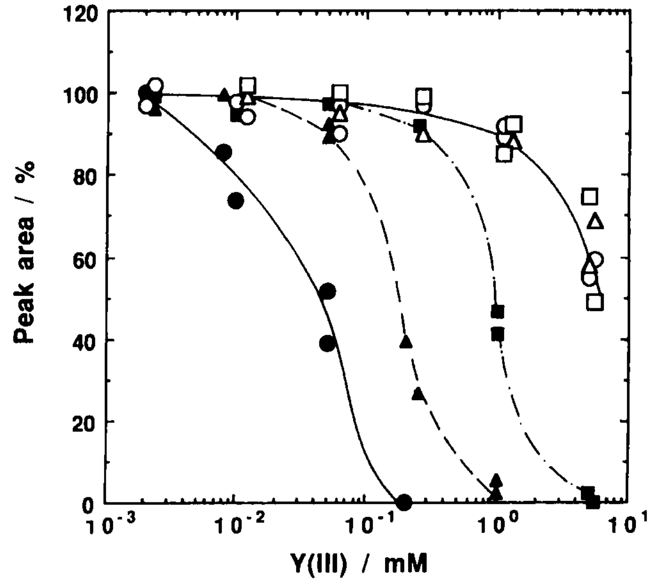

Figure 6 Interference from Y(III) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F⁻ ion.
Without pretreatment: ●, 0.2 mM F⁻; ▲, 1.0 mM F⁻; ■, 5.0 mM F⁻.
With pretreatment: ○, 0.2 mM F⁻; △, 1.0 mM F⁻; □, 5.0 mM F⁻.

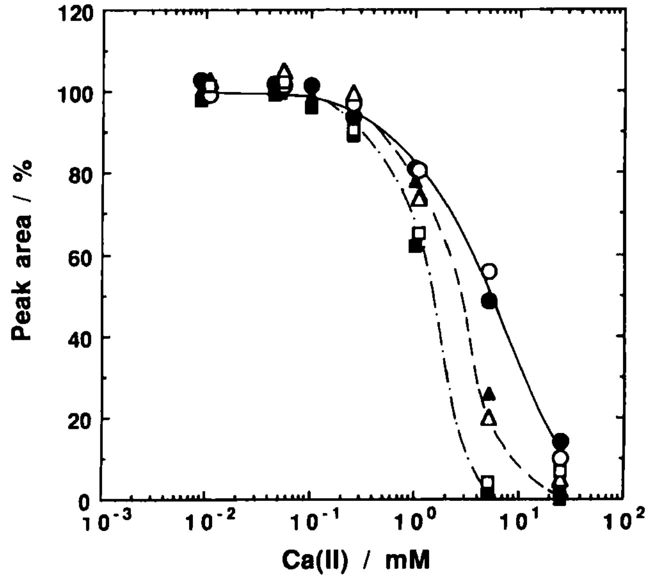

Figure 7 Interference from Ca(II) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F⁻ ion.
Without pretreatment: ●, 0.2 mM F⁻; ▲, 1.0 mM F⁻; ■, 5.0 mM F⁻.
With pretreatment: ○, 0.2 mM F⁻; △, 1.0 mM F⁻; □, 5.0 mM F⁻.

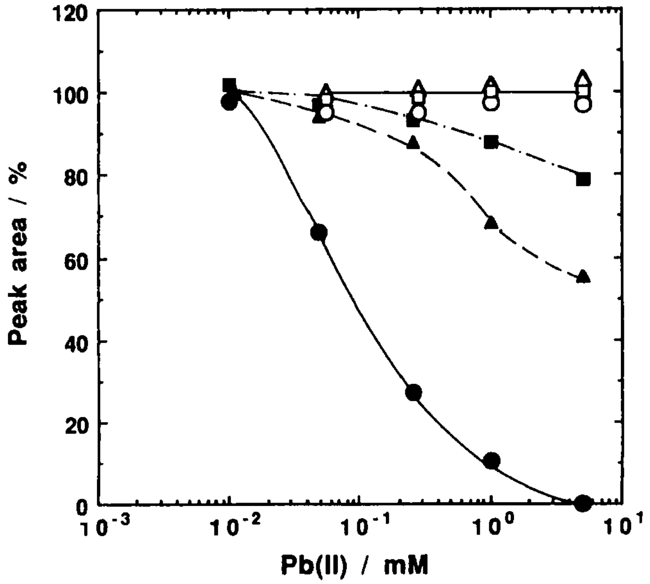

Figure 8 Interference from Pb(II) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F^- ion.
Without pretreatment: ●, 0.2 mM F^-; ▲, 1.0 mM F^-; ■, 5.0 mM F^-.
With pretreatment: ○, 0.2 mM F^-; △, 1.0 mM F^-; □, 5.0 mM F^-.

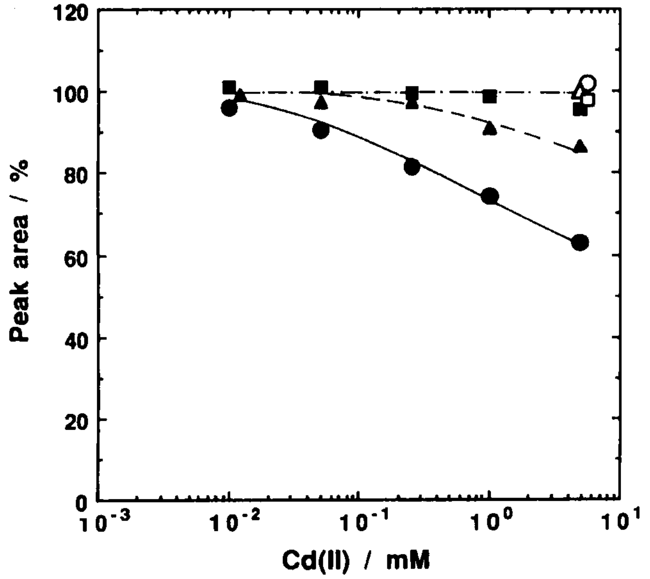

Figure 9 Interference from Cd(II) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F^- ion.
Without pretreatment: ●, 0.2 mM F^-; ▲, 1.0 mM F^-; ■, 5.0 mM F^-.
With pretreatment: ○, 0.2 mM F^-; △, 1.0 mM F^-; □, 5.0 mM F^-.

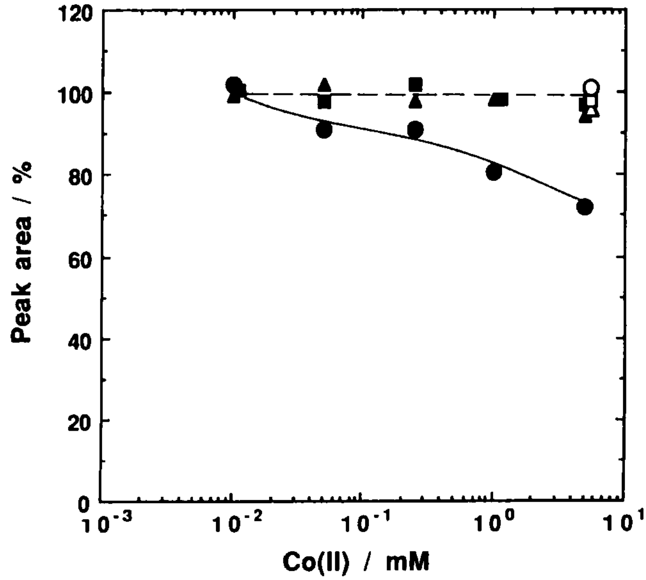

Figure 10 Interference from Co(II) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F⁻ ion.
Without pretreatment: ●, 0.2 mM F⁻; ▲, 1.0 mM F⁻; ■, 5.0 mM F⁻.
With pretreatment: ○, 0.2 mM F⁻; △, 1.0 mM F⁻; □, 5.0 mM F⁻.

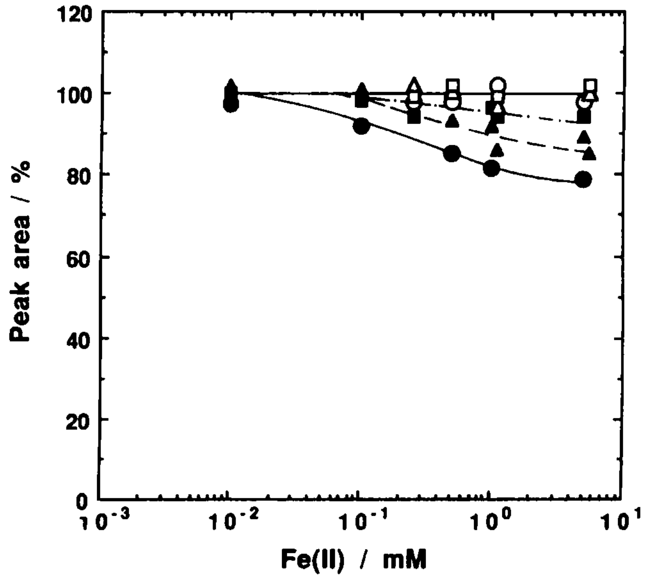

Figure 11 Interference from Fe(II) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F⁻ ion.
Without pretreatment: ●, 0.2 mM F⁻; ▲, 1.0 mM F⁻; ■, 5.0 mM F⁻.
With pretreatment: ○, 0.2 mM F⁻; △, 1.0 mM F⁻; □, 5.0 mM F⁻.

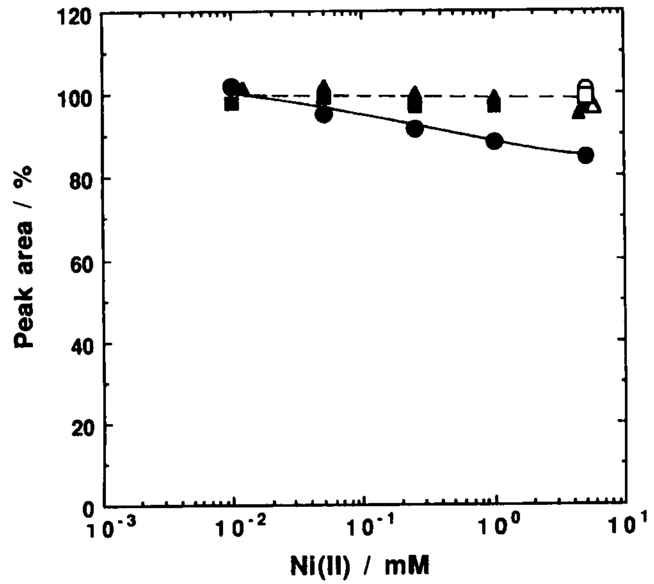

Figure 12 Interference from Ni(II) ion and its elimination by alkali pretreatment. Peak areas are normalized with those of corresponding metal-free F^- ion.
Without pretreatment: ●, 0.2 mM F^-; ▲, 1.0 mM F^-; ■, 5.0 mM F^-.
With pretreatment: ○, 0.2 mM F^-; △, 1.0 mM F^-; □, 5.0 mM F^-.

Alkali pretreatment

The effect of pH on the chromatogram peak areas of F^- ion are shown in Figure 13 for metal-free 1.0-mM F^-, 1.0-mM F^- + 0.2-mM Al(III) and 1.0-mM F^- + 0.2-mM La(III) solutions. In absence of metal ions, the F^- peaks are almost constant in the pH range from 4 to 11. At pH higher than 11, the F^- peak increases abruptly. In presence of 0.2-mM Al(III) at neutral pH, the F^- peaks are approximately half of those of the metal-free F^- ion. Under the presence of 0.2-mM La(III), the F^- peaks are lower than those under the existence of Al(III) ion at pH 11 or below. However, by adjusting the pH at around 12.3, the F^- peaks increase dramatically to almost equal levels to those of the metal-free F^- ion. Therefore, it is indicated that it is possible to eliminate the interference from those metal ions only by adjusting pH of the F^- solutions.

The chromatograms of alkalified metal-free 1.0-mM F^-, 1.0-mM F^- + 0.25-mM Al(III) and 1.0-mM F^- + 1.0-mM Al(III) solutions are shown in Figures 14 A, B and C, respectively. In the metal-free 1.0-mM F^- (Figure 14 A), the system peak at the beginning of the chromatogram is distorted significantly and the water dip which can be seen in Figure 1 disappears. Although the base line is raised slightly because of such a high positive system peak, a sharp F^- peak can be detected at the same retention time as that of F^- ion without pH adjustment. Similarly, in presence of 0.25-mM Al(III) ion (Figure 14 B), a distortion of the system peak and a raise in the base line can be seen. But in comparison with Figure 1 B, the decrease in the peak area is much less, indicating that the Al(III) interference is reduced. Finally, in Figure 14 C, a clear F^- peak can be seen even in presence of 1.0-mM Al(III) ion which cannot be detected without the alkali pretreatment.

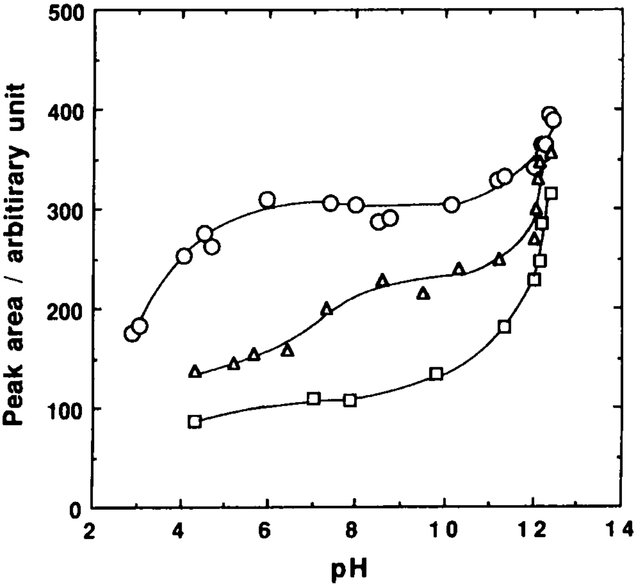

Figure 13 Effect of pH on F⁻ peak areas.
○, 1.0 mM F⁻; △, 1.0 mM F⁻ + 0.2 mM Al(III); □, 5.0 mM F⁻ + 0.2 mM La(III).

An aliquot of the same F⁻-metal solutions as those used in the above discussion were alkalified at pH 12.3. Precipitation of hydroxide was not observed in the samples containing Al(III) ion at such a high pH because of the formation of soluble species, $Al(OH)_4^-$. But in the case of the samples containing the other metal ions, precipitation of the metal hydroxide was observed especially at high metal concentrations. The precipitates were removed by filtration prior to analysis. The results of the F⁻ determination with such alkali pretreatment are shown in Figures 2 to 12 with blank marks together with the results obtained without the pretreatment which are shown with solid marks. In all cases, the metal interference are considerably reduced by the alkali pretreatment. Peak areas of more than 90% can be obtained in presence of up to 0.25 mM of Al(III), La(III) and Y(III); 1.0 mM of Ce(IV); and 2.5 mM of Ce(III). Even in presence of as high as 5.0 mM of those metal ions, F⁻ peaks can be detected. But the F⁻ peaks decrease significantly when the metal concentrations are higher than the above levels.

No effect of the alkali pretreatment was observed for the Ca(II) interference (Figure 7, blank marks). On the other hand, as shown in Figures 8 to 12 (blank marks), the interference from Pb(II), Cd(II), Co(II), Fe(II) and Ni(II) ions can be eliminated almost completely by the alkali pretreatment even in presence of 5.0 mM of those metal ions.

Effect of alkali pretreatment

The effectiveness of the alkali pretreatment can be attributed to the stability constants of metal hydroxides which are higher than those of metal fluorides except in the case of

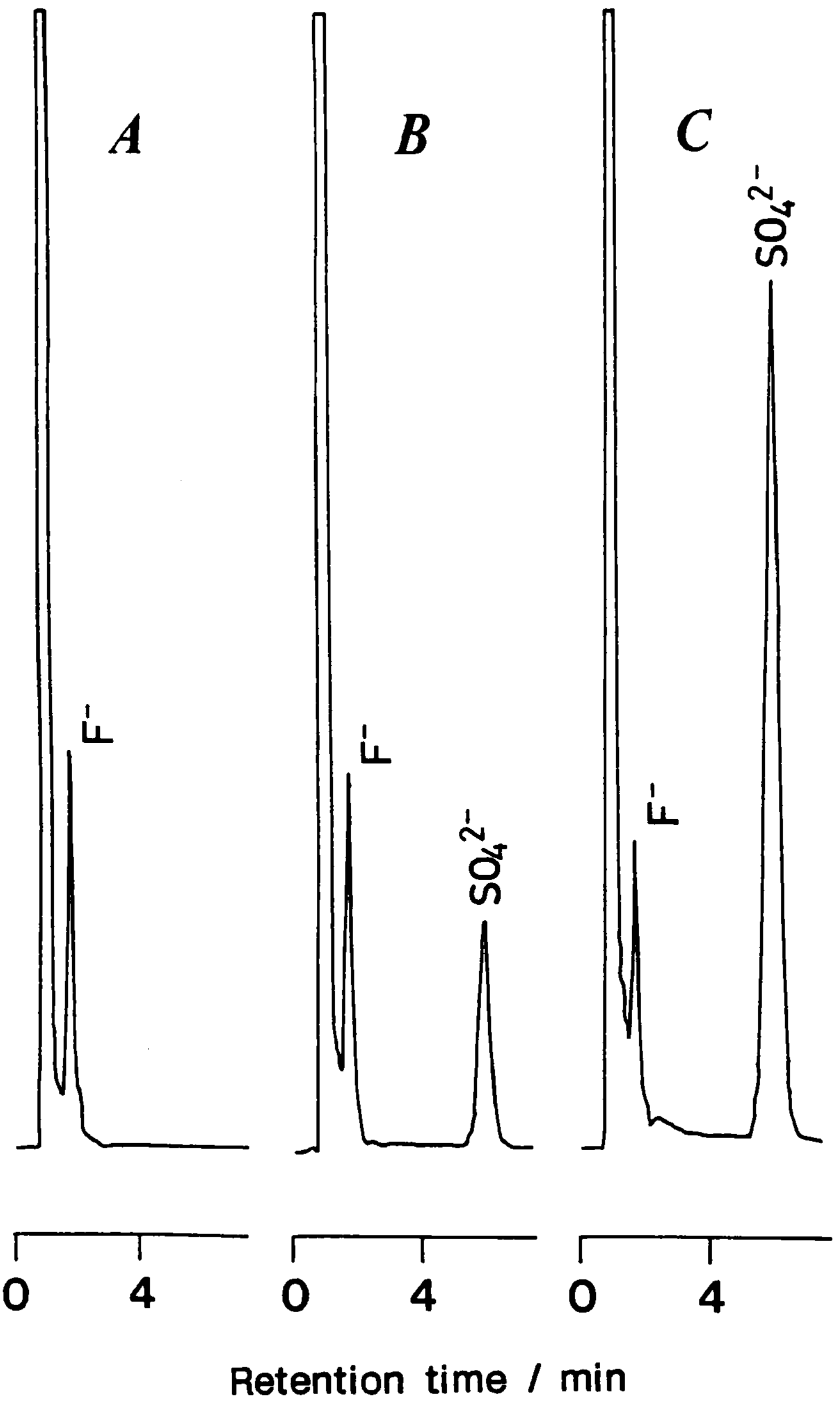

Figure 14 Chromatograms of F⁻ ion in the presence of Al(III) ion; with alkali pretreatment.
F⁻: 1.0 mM.
Al(III): (A), 0 mM; (B), 0.25 mM; (C), 1.0 mM.

Ca(II). The stability constants of hydroxides and fluorides of various metal elements are summarized in Table 1[11,12]. The very high values for the fluorides of Al(III), Ca(II), Ce(III), Ce(IV), La(III), Pb(II) and Y(III) are the major cause of the serious interferences observed in the determination of F^- ion in presence of these metal ions. As shown in Eq. (1), the more stable metal hydroxide, $M(OH)_n$, is formed by the addition of an excess amount of hydroxide ion to metal fluoride, MF_n. The released F^- ion can be detected by ion chromatography.

$$MF_n + nOH^- \rightarrow M(OH)_n + nF^- \qquad (1)$$

M: a metal element of valence n

Ineffectiveness of the alkali pretreatment for the Ca(II) interference can be attributed to the fact that the stability constant of $Ca(OH)_2$ is lower than that of CaF_2. Therefore, the addition of an excess amount of hydroxide ion does not convert CaF_2 to $Ca(OH)_2$ and consequently no free F^- ion is released from calcium fluoride.

The effect of injecting samples of high pH value to the separation column was studied. Since it was impossible to measure the pH value inside the column, the measurement was made of the eluent collected from the inlet portion of the column by disconnecting the column joint. Practically, the eluent was introduced into a glass tube (14.5 mm i.d. x 50 mm high) where a pH electrode (12 mm o.d.) was dipped, and was drained from the top. When a 20 μl of NaOH solution (pH 12.3) was injected, the pH reading began to increase 1.4 min after the injection, reached the highest value of 4.33 after 2.0 min and decreased to its initial value, pH 4.11, after 4.0 min. Thus, the injection of the alkaline samples insignificantly changes the pH of the eluent due to the strong buffer action of the eluent.

At such a low pH value as 4.33 or less, there is a possibility that the released F^- ion at pH 12.3 may recombine with the metal ion which results in the reduction of the F^- peak. This can be seen when concentrations of Al(III), Ce(III), Ce(IV), La(III) and Y(III) ions exceed a certain level, where F^- peaks are affected significantly even with the alkali pretreatment. But the rate of F^- ion to recombine with metal ion seems slow enough at lower metal ion levels since the alkali pretreatment has effectively eliminated the metal interference.

Table 1 Stability constants for metal hydroxides and fluorides at 25°C for an equilibrium $ML_n/M{\bullet}L^n$ unless otherwise mentioned[11].

Metal	*Hydroxide*	*Equilibrium*	*Fluoride*	*Equilibrium*
Al(III)	33.5	–	16.7	–
Ca(II)	5.19	–	10.41	–
Cd(II)	14.35	–	0.53	–
Ce(III)	21.2	–	4.0	ML/M•L
Ce(IV)	54.5	$M_2L_4/M^2{\bullet}L^4$	8.16*	ML/M•L
Co(II)	14.9	–	0.4	ML/M•L
Fe(II)	15.1	–	0.8	ML/M•L
La(III)	20.7	–	3.6	ML/M•L
Ni(II)	8	–	0.5	ML/M•L
Pb(II)	10.9	–	7.44	–
Y(III)	23.2	–	12.1	$ML_3/M{\bullet}L^3$

* This value is from reference 12.

Repeatability

The determination of F⁻ ion with the alkali pretreatment was repeated on 0.2-, 1.0- and 5.0-mM F⁻ solutions in absence of metal ions and in presence of 0.25-mM Al(III) and 0.25-mM La(III). The results are shown in Table 2. The repeatabilities for the metal-free F⁻ solutions are as high as 2.38 to 2.74%. Even in presence of 0.25-mM Al(III) or La(III) ion the repeatabilities are very high, 1.99 to 6.20%. Therefore, it can be concluded that the alkali pretreatment is very effective to eliminate metal interferences when the metal ion concentrations are lower than a certain level mentioned in the previous section. On the other hand, no adverse effects have been found in the life and the performance of the separation column for a period of more than three years of operation.

CONCLUSION

Metal ions such as Al(III), Ce(III), Ce(IV), La(III) and Y(III) cause very serious interferences in the determination of low concentrations of F⁻ ion by ion chromatography. Negative interferences become appreciable on 0.2-mM F⁻ at 0.01- to 0.02-mM Al(III), Ce(IV), La(III), Y(III) and Ce(III). When these metal ions exist at higher concentrations than that of F⁻ ion, the F⁻ peaks almost disappear. The interference from these metal ions is more significant on lower concentration of F⁻ ion. The interference from Ca(II) becomes significant from 0.25 mM, and slightly more serious on higher concentration of F⁻. The interference from Pb(II) is less serious than those of the above metal ions and becomes appreciable at 0.02 mM for 0.2-mM F⁻, 0.05 mM for 1.0-mM F⁻ and 0.25-mM for 5.0-mM F⁻. The interference from Cd(II), Co(II), Fe(II) and Ni(II) ions are less significant.

By adjusting the pH at 12.3, the metal interference can be effectively reduced. Peak areas of 90% or higher are obtained in presence of less than 0.25 mM of Al(III), La(III) and Y(III); 1.0 mM of Ce(IV); and 2.5 mM of Ce(III) ions. The interference from Pb(II), Cd(II), Co(II), Fe(II) and Ni(II) can be eliminated almost completely even in presence of 5.0 mM of those metal ions. However, the alkali pretreatment is ineffective for the Ca(II) interference. The effectiveness of the alkali pretreatment can be attributed to the higher stability constants of metal hyroxides than those of metal fluorides. This pretreatment enables efficient determination of F⁻ by the ion chromatography with a repeatability between 1.99 and 6.20%.

Table 2 Repeatability of the measurement with the alkali pretreatment.

Fluoride mM	*Metal mM*	*No. of reptn.*	*Mean peak area*	*Percentage to standard*	*Coeff. of variation %*
0.2	–	17	82.8	–	2.74
1.0	–	16	341.1	–	2.38
5.0	–	16	1726.0	–	2.43
0.2	0.25Al(III)	10	83.7	101.1	6.20
1.0	0.25Al(III)	20	313.5	91.8	5.17
5.0	0.25Al(III)	10	1594.3	92.4	4.92
0.2	0.25La(III)	10	76.8	92.8	5.02
1.0	0.25La(III)	20	334.4	97.9	2.96
5.0	0.25La(III)	10	1648.6	95.5	1.99

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