Notes

Evaluation of a Complexation Solid-Phase Extraction Method for Eliminating Interferences Caused by Metal Ions in the Determination of Fluoride Ion in Water

Hiroki KUMAGAI[†], Ikuko TAJIMA, Tetsushi SAKAI and Yoshinori INOUE

Division of R&D, Yokogawa Analytical Systems Inc., Musashino, Tokyo 180, Japan

Keywords Fluoride ion, ion chromatography, postcolumn derivatization, lanthanum-Alizarin complexon, solid phase extraction, complexation, 8-quinolinol

For the determination of fluoride ion in water, absorptiometry and ion chromatography (IC) have been prescribed in several standard methods.¹⁻³ Absorptiometry with Alizarin complexone (ALC) is widely used for the determination of fluoride.^{4,5} However, in order to avoid interference, it is necessary that the sample solution is treated by some method, such as distillation¹⁻³ or micro diffusion.^{6,7} Although IC is known as a good separation method for inorganic ions, some interference arises from co-eluting substances, such as borate, silicate, formate and acetate, in the determination of fluoride ion. For eliminating such interference, postcolumn derivatization methods with lanthanum-ALC⁸, 8-hydroxyquinoline sulfonate⁹ and Xylenol Orange¹⁰ have been reported. However, interference caused by metal ions cannot be completely avoided by using the above mentioned method.

We report here on an effective method for eliminating interference caused by metal ions in the determination of fluoride ion by IC with postcolumn derivatization.

Experimental

Reagents

All of the reagents were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). The lanthanum-ALC solution was prepared by dissolving Alfusone® (Dojin Chemical Ltd., Kumamoto, Japan) in a mixed solution of acetone and water. The pH of the reagent was adjusted with acetic acid or a 25% ammonia solution.

A 1000 mg l⁻¹ fluoride standard solution was prepared by dissolving 0.221 g of sodium fluoride in 100 ml of pure water. This solution was stored in a polypropylene bottle in a refrigerator. An analytical fluoride solution was prepared by diluting the 1000 mg l⁻¹ stock solution so as to have an adequate fluoride concentration.

Ion chromatography (IC) and other equipment

The ion chromatograph used in this experiment was a Model IC7000S (Yokogawa Analytical Systems Inc., Tokyo, Japan) equipped with a column oven, a chemical reactor, a conductometric detector and a variable-wavelength UV/VIS detector. A Model LC100P pump (Yokogawa Analytical Systems Inc.) was used for delivering the postcolumn reagent.

Excelpak ICS-A23 and ICS-A2G (Yokogawa Analytical Systems Inc.) were used as the separation column. The ICS-A23 column was 75 mm×4.6 mm i.d., packed with a hydrophilic anion exchange resin (ion exchange capacity of 0.05 meq g⁻¹ of dry). The ICS-A2G was a guard column for the ICS-A23. The ion chromatograph was operated under the following conditions: mobile phase of 3×10⁻³ mol l⁻¹ sodium carbonate at a flow rate of 1.0 ml min⁻¹, the scavenger of 0.015 mol l⁻¹ sulfonic acid with a flow rate of 1.0 ml min⁻¹, column temperature of 40°C, and an injection volume of 0.05 ml. Poly[ethylenetetrafluoroethylene] tubing was employed as the reaction coil.

For determining the fluoride ion by absorption spectroscopy and measuring the spectrum of the dye compound, a Model 8452A diode array spectrophotometer (Hewlett-Packard Co., Germany) unit was used.

Solid-phase extraction cartridge

A TOYOPAK ODS-M (TOSO Co., Tokyo, Japan) and an Excelpak SPE-GLF (Yokogawa Analytical Systems Inc.) were used for the solid-phase extraction (SPE) cartridge. The TOYOPAK ODS-M cartridge was packed with 300 mg of octadecyl group bonded silica gel. The Excelpak SPE-GLF cartridge was packed with 500 mg of hydrophobic porous polymer. These SPE cartridges were washed with 5 ml methanol and 10 ml pure water before use.

Results and Discussion

The postcolumn derivatization conditions were op-

[†] To whom correspondence should be addressed.

timized based on a previous report.⁸ The optimized conditions are given in Table 1. Under this condition, the detection limit ($S/N=3$) for fluoride ion was 0.02 mg l^{-1} . The RSD at 0.1 mg l^{-1} of fluoride ion was 2.7% ($n=10$).

In lanthanum-ALC absorptiometry the interference of ions *i.e.* iron, aluminum, bicarbonate, chloride, bromide, nitrate, sulfonate, have been reported.¹⁻³ A concentration of anions 10^3 to 10^4 times higher than the fluoride ion concentration is tolerable. However, the interference of metal ions is a more serious problem.

The recovery of fluoride ion in the presence of various inorganic ions and organic acids is described in Table 2; 0.1 mg l^{-1} of fluoride ion solutions containing various ions were used as test solutions. Inorganic anions and organic acid concentrations of up to 10 mg l^{-1} did not interfere with the fluoride ion determination. Metal ions, except for aluminum, gave the same results as did solutions containing anions. The interference of aluminum was very large compared with that of other metal ions. This is not an unexpected result considering the relatively high stability constants of aluminum-fluoro complexes.

Table 1 Optimized operating conditions

Instrument	Model IC7000S and Model LC100P
Column	Excelpak ICS-A2G/ICS-A23 25 mm×2.7 mm i.d./ 75 mm×4.6 mm i.d.
Column temperature	40°C
Mobile phase	$3 \times 10^{-3} \text{ mol l}^{-1} \text{ Na}_2\text{CO}_3$
Flow rate	1.0 ml min^{-1}
Scavenger	$15 \times 10^{-3} \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$
Flow rate	1.0 ml min^{-1}
Reagent	4% lanthanum-ALC in 30% acetone/water, pH 4.5
Flow rate	0.5 ml min^{-1}
Reaction coil	2 m×0.5 mm i.d.
Reaction temp.	60°C
Detection	conductmetric and visible photometric (660 nm)
Injection volume	0.05 ml

Since the interference of aluminum was a serious problem for a direct determination of fluoride ion, coexisting aluminum should be removed by some pretreatment method before an analysis. Although aluminum forms very stable complexes, such as AlF_2^+ , AlF_2^+ and AlF_6^{3-} , by complexation with fluoride ion, these complexes are decomposed by 8-quinolinol and a new complex is formed with 8-quinolinol. The extractive separation of metal ions using 8-quinolinol has been reported.¹³

The SPE method combined with 8-quinolinol complexation was examined in order to remove any coexisting aluminum. TOYOPAK ODS and Excelpak SPE-GLF were used as a reversed phase SPE cartridge for removing aluminum-8-quinolinol complex. An 8-quinolinol methanol solution was added to 0.1 mg l^{-1} fluoride ion containing various concentrations of aluminum. The final concentration of 8-quinolinol was kept at 0.1%. The pH of the mixture was adjusted 7.38. Subsequently, the mixture solution was stirred for 30 min in order to complete the complexation with aluminum. The resultant complex was removed by the SPE cartridge and the eluate from the SPE cartridge was analyzed by the postcolumn-IC method.

The SPE method combined with 8-quinolinol complexation was examined in order to remove any coexisting aluminum. TOYOPAK ODS and Excelpak SPE-GLF were used as a reversed phase SPE cartridge for removing the aluminum-8-quinolinol complex. The procedure of aluminum-8-quinolinol complex formation was followed in a previous report.¹³ An 8-quinolinol methanol solution was added to 0.1 mg l^{-1} fluoride ion containing various concentrations of aluminum. The concentration of 8-quinolinol was maintained at 0.1%. Subsequently, the mixture solution was stirred for 30 min in order to complete the complexation with aluminum. A sample solution containing aluminum-8-quinolinol complex was manually passed through the SPE cartridge using a disposable syringe. The eluate from the SPE cartridge was analyzed by the postcolumn-IC method.

Table 3 describes the recovery of fluoride ion from a sample solution containing various concentrations of aluminum. When SPE-GLF was used, recoveries greater than 95% were obtained, even when 10 mg l^{-1} of

Table 2 Interference of coexisting ions on the recovery of 0.1 mg l^{-1} fluoride

Ion	Concentration/ mg l^{-1}	Recovery, %	Ion	Concentration/ mg l^{-1}	Recovery, %	Ion	Concentration/ mg l^{-1}	Recovery, %
Cl^-	10	101	ClO_4^-	10	98	Fe(III)	10	99
Br^-	10	98	IO_3^-	10	100	Co(II)	10	99
NO_2^-	10	98	B^a	10	95	Ni(II)	10	96
NO_3^-	10	106	Si^b	10	101	Cd(II)	10	96
PO_2^-	10	95	Al(III)	0.01	101	Pb(II)	10	98
PO_4^{3-}	10	102		0.1	96	Formate	10	106
SO_3^{2-}	10	96		1	75	Acetate	10	102
SO_4^{2-}	10	103		10	27	Propionate	10	100

a. Added as borate. b. Added as sodium silicate.

Table 3 The recovery of fluoride ion by SPE method using complexation under various aluminum concentration

Added concentration of aluminum/mg l ⁻¹	Recovery, %	
	ODS	SPE-GLF
0.01	87.9	98.2
0.1	87.3	98.6
1	88.6	101.7
2	90.9	103.5
5	90.6	104.1
10	90.0	95.8

Fig. 1 Chromatograms of river water by the conductometric detection method (A) and the postcolumn derivatization method (B). The conditions are the same as those given in Table 1. Peaks: 1, fluoride; 2, chloride; 3, nitrite; 4, bromide; 5, nitrate; 6, phosphate; 7, sulfate.

aluminum was added. The recovery of fluoride ion by ODS was less than that by SPE-GLF packed with a polymer gel. Although the reason for this result has not been investigated well, it is likely that fluoride ion interacted with the silica gel.

The SPE method using complexation with 8-

quinolinol would avoid the interference of other metal ions as well as aluminum because of its complex-forming ability.^{14,15} Furthermore, this SPE method would be useful for the simultaneous determination of other inorganic anions as well as fluoride ion, because the sample solution is not contaminated by a pretreatment.

Figure 1 shows chromatograms of river water obtained by the postcolumn derivatization method with conductometric detection. It is clear that organic acids, such as formate and acetate, interfered with determining fluoride ion in conductometric detection. On the contrary, such interference was not observed in the postcolumn derivatization method. In Fig. 1, the determined concentration of fluoride ion is given as 0.12 mg l⁻¹.

References

1. JIS K 0101 "Testing methods for industrial water", Japanese Industrial Standards Committee, Tokyo, 1991.
2. JIS K 0102 "Testing methods for industrial waste water", Japanese Industrial Standards Committee, Tokyo, 1993.
3. "Standard methods for the examination of water", Japan Water Works Association, Tokyo, 1993.
4. R. Belcher, M. A. Leonard and T. S. West, *J. Chem. Soc.*, **1958**, 2390.
5. R. Belcher and M. A. Leonard, *J. Chem. Soc.*, **1960**, 3577.
6. D. R. Taves, *Talanta*, **15**, 965, 1015 (1968).
7. R. Sara and E. Wäninen, *Talanta*, **22**, 1033 (1975).
8. M. Matsui, M. Nishikawa and M. Morita, *J. Environ. Chem.*, **4**, 665 (1994).
9. P. Jones, *Anal. Chim. Acta*, **258**, 123 (1992).
10. N. W. Barnett, P. Johnes and H. W. Handley, *Anal. Lett.*, **26**, 2525 (1993).
11. R. Greenhalgh and J. P. Riley, *Anal. Chim. Acta*, **25**, 179 (1961).
12. H. Wada, H. Mori and G. Nakagawa, *Anal. Chim. Acta*, **172**, 297 (1985).
13. R. Belcher and T. S. West, *Talanta*, **8**, 853 (1961).
14. M. Blanco, J. Coello, F. Gonzalez, H. Iturriaga and S. Maspoch, *Anal. Chim. Acta*, **226**, 271 (1989).
15. K. Motoshima and H. Hashitani, *Bunseki Kagaku*, **9**, 151 (1960).

(Received June 7, 1995)

(Accepted September 18, 1995)