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By

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Introduction.

The recent development of fluorine chemistry has called much more attention to the quantitative determination of fluoride ion. Although many methods, including gravimetry, volumetry and colorimetry, have been devised for this purpose, none of them can be applied without separating fluoride ion, prior to its determination, from interfering ions. This may be accomplished by converting fluoride ion into fluosilicic acid followed by distillation, as was proposed by Willard and Winter1) in 1933, and this seems to be the only one method that has been put in practice.

The ions which generally interfere the determination of fluorine are PO_4^{3-}, AsO_4^{3-}, SO_4^{2-} and CO_3^{2-}. According to the affinities for anion exchange resin, these polyvalent ions are more easily adsorbed by the resin than univalent ions, and fluoride ion is less readily adsorbed than any other univalent ion. This means that fluoride must be the first ion to be eluted from the resin in ion exchange chromatography, suggesting that this type of chromatography might be a new method of separation of fluoride from other ions.

The object of this research was to test an applicability of anion exchange resin to separation of fluoride ion, and that of cation exchange resin is not mentioned here, as it has already been reported by H. Shimizu2) and M. Honda.3)

Experimental Results and Considerations.

1. With anion exchange resin of R–Cl type.

A glass column, 7 cm. in diameter and 20 cm. in height, provided with a glass stopper at the bottom, was filled with Amberlite IRA-400 (about 100 mesh) to a height of 15 cm. The solutions containing both fluoride and interfering ions were passed through the column at a flow rate of about 1 ml./min., and the ions adsorbed were eluted in the manner described below. The regeneration of the resin was affected by passing 10% NaCl solution through it. For the determination of fluoride ion, the

$AlCl_3$-titration,[4] with Eriochromocyanine R as indicator, was used.

a. Separation of $F^-$from PO_4^{3-}.

By passing NaCl solutions of various concentrations through the resin column, in which 2 ml. of 0.1N Na_3PO_4 or 1.5 ml. of 0.1N NaF solution had been adsorbed, it was found that ca. 120 ml. of 0.2% or ca. 40 ml. of 0.5% NaCl solutions was necessary for PO_4^{3-} to be detected in the eluate, and that ca. 40 ml. of 0.2% NaCl solution was enough to elute almost all of F^-.

It may be deduced, therefore, that by using 0.2% NaCl solution as the eluant, F^- can be separated from PO_4^{3-}. The results of the experiments on separation of F^- from PO_4^{3-} are shown in Table 1.

Table 1.

Interfering Ion	Sample Taken as F^- (a)	Measurement Fouhd as F^- (b)	(b/a)×100 %
PO_4^{3-}	0.015 meq	0.0148 meq	98.7
	〃	0.0149	99.3
	〃	0.0144	96.0
	〃	0.0147	98.0

On account of the inferior adsorption of $H_2PO_4^-$ or HPO_4^{2-} to PO_4^{3-}, they were converted into HPO_4^{2-} and PO_4^{3-} by adjustment of the pH of the solutions at 9 or 12. Table 2 shows the results of the experiments on separation of F^- from $H_2PO_4^-$.

Table 2.

Interfering Ion	pH Adjusted	Sample Taken as F^- (a)	Measurement Found as F^- (b)	(b/a)×100 %
$H_2PO_4^-$	9	0.015 meq	0.0150 meq	100.0
	〃	〃	0.0149	99.3
	12	〃	0.0147	98.0
	〃	〃	0.0149	99.3

b. Separation of F^- from SO_4^{2-} and CO_3^{2-}.

Table 3 shows the results of the experiments on removal of SO_4^{2-} and CO_3^{2-} from F^-, carried out by operating as above.

Table 3.

Interfering Ions	Sample Taken as F^- (a)	Measurement Found as F^- (b)	(b/a)×100 %
SO_4^{2-}	0.015 meq	0.0148 meq	98.7
〃	〃	0.0148	98.7
CO_3^{2-}	0.015 meq	0.0147	98.0
〃	〃	0.0149	99.3

As clearly shown in Table 3, fluoride ion was separated, with fair accuracy, from these interfering ions at the concentration of F^- of about 0.1 mg./ml. It seems, therefore, that this method of separation may be a very convenient for routine analysis. But a slight leakage of F^-, which would be larger at higher concentrations of interfering ions, might sometimes be a defect of this method. When 5 ml. of a mixture of 0.015N NaF and 0.1N NaCl solutions was passed through the column, for instance, it was observed that about 15% of F^- leaked out without being adsorbed. According to H. Shimizu,[5] 0.5 ppm. of F^- may leak out when natural water containing F^- is passed through an anion exchange resin of R–Cl type. In such a case, therefore, not only the fluoride ion in the eluate, but also that in the first effluent must be determined.

2. With anion exchange resion of R–OH type.

Conversion of fluoride into HF by treatment of the sample with R–H type cation exchanger followed by adsorption of the HF by R–OH type anion exchanger would furnish an obviously possible means to prevent leakage of F^-. But this necessitates a two-step treatment and invites, moreover, difficulty of quantitative recovery of F^- without a sufficient washing of the cation exchanger. The simple application of a strongly basic anion exchange resin was therefore studied. The resin used was Amberlite IRA–410.

a. Leakage of F^-.

To find the effects of the concentration of interfering ions upon leakage of F^-, 0.01–0.1N NaCl solutions containing 0.1 mg. of F^- per 1 ml. was prepared, 10 ml. of each solution was passed through the R–Cl or R–OH type resin column, and the fluoride ion was eluted by 50 ml. of 0.2% NaCl solution or of 0.1N NaOH solution.

Table 4.

Form of Resin	Concentration of NaCl	F–Found in Effluent	F–Found in Effluate
R–OH	0.01 N	4 γ	1.04 mg
R–Cl	〃	5	1.00
R–OH	0.02	0	1.04
〃	0.03	3	1.01
R–Cl	〃	5	1.02
R–OH	0.05	5	1.03
〃	〃	7	1.05
R–Cl	〃	98	0.92
R–OH	〃	3	0.98
〃	〃	—	0.95
〃	0.1	—	0.96
R–Cl	〃	>70	0.85

Sample taken, 1mg as F^-

Table 5.

Conc. of NaCl	Conc. of F^-	Sample Taken as F^-	F^- Found in Effluent	F^- Found in Effluate
0.05 N	5 ppm	125 γ	6.3 γ	124 γ
"	"	"	6.1	"
"	10	100	2.0	96
"	"	"	0	—
"	1	50	3.5	47
"	"	"	1.2	—

The results of the determination of F^- in the effluent and in the eluate are shown in Table 4 and Table 5.

For the determination of F^-, Ferric-Salicylate or Thorium-Alizarin photoelectric colorimetry was used, the latter being applied when the concentration of F^- was less than 10 ppm.

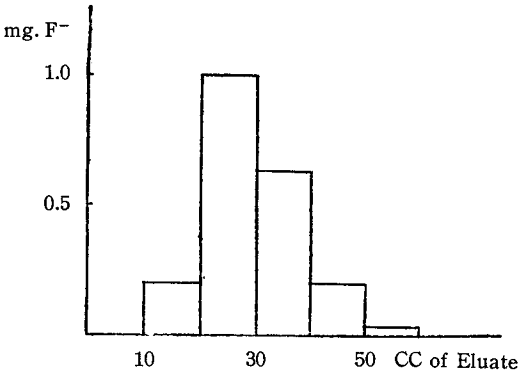
i. Photoelectric determination with Ferric-Salicylate.[6]

Prepare Fe-Salicylate solution by mixing equal volumes of 2×10^{-3} mol./l. $FeCl_3$ solution (containing 0.1N HCl) and of 2×10^{-3} mol./l. Na-Salicylate solution. After adding an adequate quantity of a standard NaF solution to 10 ml. of the mixture, dilute it to 50 ml. with water, and measure the percent transmittancy at 530μm.

ii. Photoelectric determination with Thorium-Alizarin.[7]

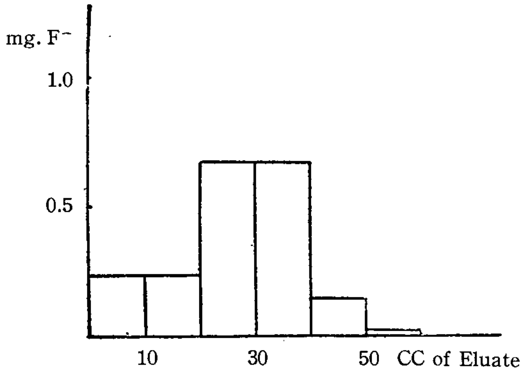
Mix 10 ml. of 0.1N $Th(NO_3)_4$ solution, 0.5 g. of Alizarin S, 3.78 g. of $CH_2ClCOOH$ and 1.5 g. of NaOH in 1 *l*. of water, and adjust the pH of the reagent at 2.8. After two or three days, add an adequate quantity of a standard NaF solution to 10 ml. of the upper layer, and dilute it to 50 ml. for the measurement of the percent transmittancy at 530μm.

When the resin is used in R-OH form, leakage of F^- is so slight as to be negligible, as is shown in Table 4 and Table 5. Interfering cations, if present, must be previously removed with a cation exchange resin, but if no interfering cations are present, an anion exchange resin seems to be enough to remove interfering ions completely.



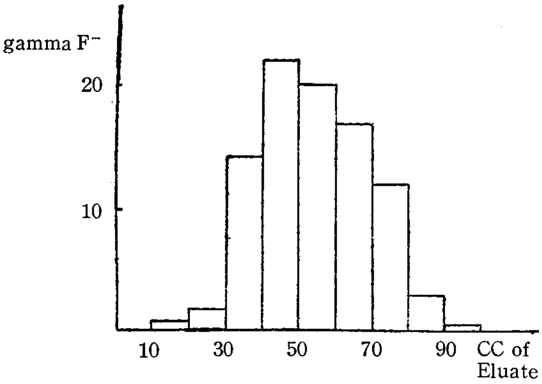
Sample taken 2.15 mg. as F^-
Interfering Ions,
PO_3^{4-} 0.15 meq.
SO_4^{2-} 0.10 meq.
Cl^- 0.10 meq.

Fig. 1.



Sample taken 2.15 mg. as F^-
Interfering Ions,
PO_4^{3-} 0.30 meq.
SO_4^{2-} 0.10 meq.
Cl^- 0.10 meq.

Fig. 2.



Sample taken 100 gamma as F^-
Interfering Ions,
PO_4^{3-} 0.2 meq.
SO_4^{2-} 0.5 meq.
Cl^- 1.0 meq.

Fig. 3.

b. Elution curve.

The elution curve in Fig. 1 was obtained by passing a known quantity of various samples (containing both F^- and interfering ions) through the resin, eluting it with 0.1N NaOH solution at a flow rate of 1 ml./min., collecting 10–20 ml. alliquots consecutively and determining the fluoride ion in it.

Fig. 1~3 show a rapid elution of F^- even at high concentrations of interfering ions. But since the quantity of the resin used in this experiment is about 5 ml., and therefore its exchange capacity is about 5 meq., it is necessary to keep the quantity of interfering ions below 0.5 meq. in order to separate F^- completely and to avoid leakage of F^- perfectly.

For the precise determination of F^-, on the other hand, it is desirable that at least 100 γ of F^- should be adsorbed. However, when the concentration of F^- is low and that of interfering ion is high, the quantity of some interfering ion may often exceed 0.5 meq. for adsorption of 100 γ of F^-. In such a case, therefore, it would be necessary to use a longer resin column such as 20 or 25 cm. in length.

c. Separation of F^- from PO_4^{3-}, SO_4^{2-}, CO_3^{2-} and Cl^-.

Among many ions which are present in natural water, PO_4^{3-}, SO_4^{2-}, CO_3^{2-} and Cl^- may interfere the determination with Fe-Salicylate or with Thorium-Alizarin. Some experiments were carried out with specially prepared sample solutions, containing a larger amount of these ions than would be in natural water, at the concentrations of F^- of 0.1 mg./ml., 10 ppm., 5 ppm. and 1 ppm. The results are shown in Table 6.

Table 6.

Interfering ions			Conc. of F^-	Sample Taken as F^-	F^- Found in Eluate
PO_4^{3-}	SO_4^{2-}	Cl^-			
0.1 meq	0.1 meq	1.0 meq	0.109 mg/cc	2.19 mg	2.20 mg
0.2	0.2	1.0	〃	〃	2.19
0.1	0.1	0.1	〃	〃	2.30
0.2	0.1	0.1	〃	〃	〃
0.3	0.1	0.1	〃	〃	2.12
0.1	0.1	0.5	〃	〃	2.16
0.05	0.125	0.25	10 ppm	250 γ	255 γ
〃	〃	〃	〃	〃	244
〃	〃	〃	〃	〃	230
〃	〃	〃	5 ppm	125 γ	128
〃	〃	〃	〃	〃	140
〃	〃	〃	〃	〃	143
0.1	0.25	0.50	〃	250 γ	243
〃	〃	〃	〃	〃	246
0.2	0.5	1.0	1 ppm	100 γ	97
0.1	0.25	0.5	〃	50 γ	48
〃	〃	〃	〃	〃	47

d. Adsorption of fluorine as SiF_6^{2-}.

In all the above cases, fluorine was adsorbed in the form of F^-. In natural water, however, much of fluorine may exist in the form of SiF_6^{2-}. The results of the experiments on adsorption and elution of Na_2SiF_6 in the presence of interfering ions, under the same conditions as mentioned above, are shown in Table 7.

Table 7.

Interfering ions			Conc. of F^-	Sample Taken as F^-	F^- Found in Eluate
PO_4^{3-}	SO_4^{2-}	Cl^-			
—	—	—	0.1 mg/cc	1.0 mg	0.976 mg
—	—	—	〃	〃	1.020
0.1 meq	0.1 meq	0.5 meq	10 ppm	250 γ	244 γ
〃	〃	〃	〃	〃	246

As is shown in Table 7, 50 ml. of 0.1N NaOH is enough for complete elution of SiF_6^{2-}, just as in the case of F^-. This must be due to the primary decomposition of fluosilicate into fluoride by the existing alkali, according to the following equation.

$$R-(NH_3)_2SiF_6+6NaOH = R-(NH_3OH)_2+SiO_2+6NaF+2H_2O.$$

Conclusion.

A new method of separation of fluoride from interfering anions has been introduced by the use of anion exchange resin. The procedure of this method is very simple, and it gives satisfactory results even when the sample contains only a slight quantity of F^-.

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