Collection of Trace Fluoride and Hydrofluoric Acid from Aqueous Samples by Calcium Hydroxyapatite

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A selective method for preconcentrating trace fluoride ions from aqueous environmental and analytical samples by calcium hydroxyapatite is described. Studies have been performed with batch and column equilibration and the optimum conditions are determined with respect to the pH, contact time and coexisting anion concentration. The addition of acetate buffer is recommended for effective uptake of fluoride. The difficulties that solid hydroxyapatite particles deform or collapse and column permeability decreases during column operations have been overcome with the use of polyacrylamide-blended hydroxyapatite. Batch procedures allow the quantitative recovery of fluoride (50–500 μg) from a 100-fold excess of aluminium ions by 1 gramme of hydroxyapatite.

INTRODUCTION

The preconcentration or removal of trace inorganic fluorides from aqueous solution is a matter of great concern in analytical and in environmental works. Most of the earlier methods for isolating fluoride included precipitation or distillation steps; however, recently interests have been directed toward the use of much simpler and effective separation techniques. Most notable of the methods is the microdiffusion technique.[1] It is highly selective and finds wider application in various fields of chemical analysis.[2–4] The limitation of the method is that it is impractical

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for recovering fluoride from a large volume of samples. Moreover, special care has to be taken to avoid the loss of volatile fluorosilane. With respect to uptake capacity, ion-exchange or adsorption seems to be very promising. A zirconium loaded cation exchange resin column method is reported to collect the low-level fluoride in natural water.[5] Solid adsorbents such as activated alumina and charcoal have extensively been used for defluoridation of water samples but they lack the selectivity. Calcium hydroxide phosphate, which is known as hydroxyapatite, belongs to one of the selective adsorbents for fluoride ion, though little attention has been paid for its analytical use. Knappwost[6] first recommended the use of calcium hydroxyapatite for microanalysis of fluoride. His titrimetric procedure, however, required also a time consuming distillation step; thus the merits of hydroxyapatite had not fully been realised. Lead strontium hydroxyapatite is apparently the other hydroxyapatite that has been applied to the determination of fluorine by photon activation.[7] Since the structure of calcium hydroxyapatite has been confirmed to be hexagonal,[8] the uptake of fluoride ion on hydroxyapatite is assumed to take place by ion-exchange.

In the present paper, we describe a successful extension of the hydroxyapatite method to the analytical and environmental problems in combination with an ion-selective electrode. The difficulties that hydroxyapatite particles deform or collapse and column permeability decreases during column operations have been overcome with the use of polyacrylamide-blended hydroxyapatite. The ease and low cost with which calcium hydroxyapatite can be prepared makes it very attractive as a collector for trace fluoride.

EXPERIMENTAL

Reagents and aparratus

Analytical reagent grade chemicals were employed in the preparation of all solutions. The water was purified by ion-exchange and distillation. Standard solution of fluoride was prepared from weighed sodium fluoride and stored in a polyethylene bottle. TISAB buffer solution (pH 5.2) was prepared by dissolving 18.6 g of potassium chloride, 36.75 g of sodium citrate and 5.7 ml of glacial acetic acid in water and diluting to 500 ml. For fluoride determination, equal volumes of the sample and the buffer were mixed.

Potentiometric measurements were made using a Corning Model 619 fluoride ion meter and a Toa Electronics Model IM—20B digital pH/ion meter at 25°C, both of which were equipped with a fluoride ion-selective electrode (Corning No. 476077 and Toa F-125, respectively) and a silver—

silver chloride reference electrode. Calibration was achieved, in the range 0.1–10 ppm F$^-$, by using known concentration of sodium fluoride standards. All pH measurements were made with a Hitachi–Horiba Model F-7 pH meter utilizing a saturated calomel—glass electrode system.

Preparation of calcium hydroxyapatite

Calcium hydroxyapatite was prepared by the method of Hayek and Stadlmann.[10] Diammonium hydrogen phosphate (39.5 g) was dissolved in 500 ml of water, and the pH was adjusted to 11 with concentrated ammonia. To the stirred phosphate solution was added a separate volume of 500 ml of calcium solution containing 118 g of calcium nitrate tetrahydrate. The reaction products were allowed to boil for about 20 min and then filtered and washed with cold water. The air-dried hydroxyapatite was powdered, sieved and the 48–100 mesh fraction was retained. Finally, it was dried for 5 hours in an electric oven at 85°C and stored over silica gel desiccant. The hydroxyapatite synthesized was identified by the qualitative comparison of X-ray diffraction spectra. Calcium and phosphate contents were determined with EDTA titration.

Modified hydroxyapatite with a loading of 15% polyacrylamide polymer was prepared for column operation. Hydroxyapatite particles (24 g) were suspended in 75 ml of aqueous solution containing 4 g of acrylamide monomer and 1 g of N, N-methylene-bis-acrylamide at 50°C; 100 mg of ammonium persulphate and 0.5 ml of 3-dimethylaminopropionitrile were then added to the stirred solution. The condensed gels were crushed in a wet state. Air-dried cakes were pulverized to approximately 48–100 mesh size particles.

Measurement of kinetics and uptake efficiency

Most of data were taken with batch methods. Weighed amounts of hydroxyapatite (usually 0.5 g) was added to 50 ml of sodium fluoride or hydrofluoric acid solution with a varying fluoride concentration. After the agitation process, the mixture was filtered through a filter paper (Toyo No. 5C). The amounts of fluoride remaining in the filtrate was determined by the ion-selective electrode method. For recovery measurement, fluoride ion taken up in the hydroxyapatite was also analyzed after dissolving it with hot 1 M hydrochloric acid. The exchange capacity data were obtained in the stirred aqueous media of a limited volume (50–150 ml) with possible variation in fluoride contents in the sample. The value of uptake capacity was expressed in m mole of fluoride ion per gramme of hydroxyapatite. The retention characteristics of fluoride ion were

examined also by a column method. Water samples were adjusted to the desired pH and passed through a 10×50 mm glass (or acrylamide) column. The effluents were then analyzed for fluoride potentiometrically. All experiments were carried out at room temperature, except for those studying the temperature effect.

RESULTS AND DISCUSSION

Influence of experimental parameters

The optimum conditions were determined with respect to the pH, contact time, particle size, temperature and the effect of coexisting anion concentration in the medium.

The percent uptake of fluoride ions measured as a function of pH is shown in Figure 1. The efficiency of fluoride removal depends on the hydrogen ion concentration of the solution. Lowering the pH of a given solution allows increasing uptake efficiency for sodium fluoride, which invariably increases the solubility for the calcium hydroxyapatite system and solid adsorbents tend to collapse. This drawback has been overcome by the use of surface-modified hydroxyapatite in batch and column processes. Kinetics of fluoride exchange on hydroxyapatite show that equilibration is attained fast and a ten-minute agitation period is sufficient for most batch applications. No effect of temperature was found in the range of 10 to 30°C. Concerning the effect of coexisting anions, it is concluded from Table I that a 100-fold excess of foreign anion concentrations does not have any effect on the uptake of fluoride at ppm levels.

Characterization of hydroxyapatite

To characterize the hydroxyapatite an analysis of its elemental composition was made. Chelatometric titration analysis reveals 37.4% Ca^{2+} and 53.2% PO_4^{3-}. Thus, Ca^{2+}/PO_4^{3-} ratio (molar basis) for synthesized hydroxyapatite is 1.66, which corresponds well with calculation based on $Ca_5(PO_4)_3(OH)$, the formula for calcium hydroxyapatite. X-ray diffraction patterns of the synthesized samples showed sharp peaks which corresponded to the three most intense bands of calcium hydroxyapatite.

Retention capacity of hydroxyapatite for fluoride ions increases with decreasing pH, reflecting the influence of pH on uptake of fluoride. The liberation of hydroxide ion resulting from uptake of fluoride ion lowers the solution pH. The apparent capacity value determined in the
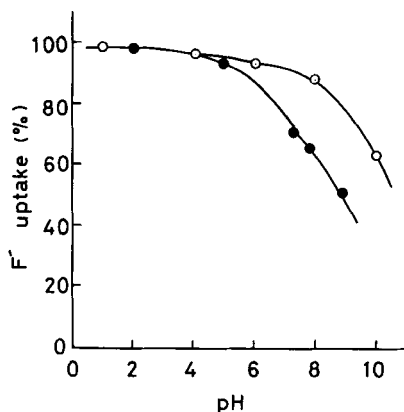
FIGURE 1   Effect of pH on uptake of fluoride.
●:Hydroxyapatite (0.25 g)—NaF solution (2500 μg F⁻/50 ml).
○:Modified Hydroxyapatite (0.30 g)—NaF solution (500 μg F⁻/50 ml).

TABLE I
Influence of coexisting anions on uptake of fluoride

		Uptake of fluoride ion (%)	
Anions[a]	Anion/F⁻ ratio	H.A.	Modified H.A.
None		97.7	95.4
Chloride	100	97.9	95.0
Bromide	100	97.7	95.4
Iodide	100	97.7	96.4
Nitrate	100	97.8	96.0
Sulphate	100	97.3	97.6
Perchlorate	100	97.3	98.7
Phosphate	100	95.6	88.2

Sample solution (sodium fluoride): 500 μg F⁻/50 ml, Hydroxyapatite (H.A.): 0.5 g, Stirring time: 30 min.

[a]Added as sodium or potassium salt.

unbuffered sodium fluoride solution was 0.35 ± 0.03 m mole g^{-1} for fluoride and the pH after 6-hr equilibration was about 7.8. This capacity value is about eight times smaller than that obtained in the acetate buffer solution (pH 4.9). The effect of acetate concentration on fluoride uptake is shown in Figure 2. In acetate media the capacity value increases with buffer concentration and reaches maximum at about 0.05 M. Thus, the
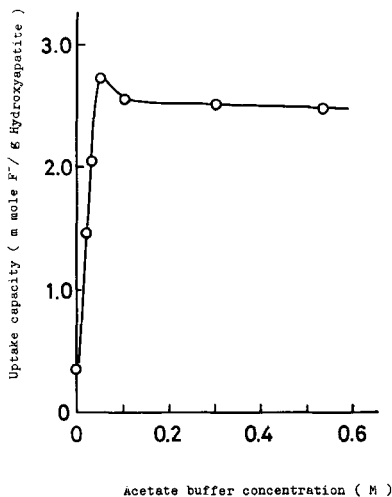
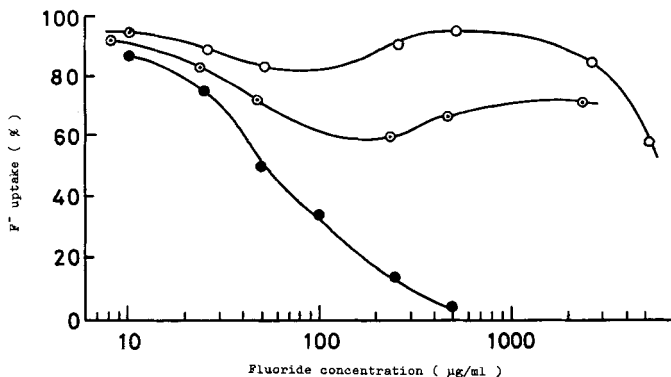FIGURE 2   Effect of buffer concentration on uptake capacity of hydroxyapatite.

FIGURE 3   Batch uptake of NaF, NH_4HF_2 and HF.
Hydroxyapatite:0.5 g, Total volume:50 ml, Stirring time:10 min:NaF (●), NH_4HF_2 (☉), HF(○).

addition of acetate buffer to the sample is recommended for effective uptake of fluoride in batch and column procedures (cf. Figure 5). The use of citrate (pH 4.4) is not suitable because partial dissolution of calcium hydroxyapatite occurs appreciably and the uptake efficiency for fluoride decreases. The complexity of the reaction mechanism imposed practical restriction on the capacity measurement for hydrofluoric acid, though the uptake of fluoride on hydroxyapatite has been assumed to take place by ion-exchange.[9] The adsorption behavior of fluoride ions differs remarkably

TABLE II

Uptake of fluoride by various calcium phosphates

	Commercial products			Synthesized products	
	A	B	C	$Ca_3(PO_4)_2$	$Ca_5(PO_4)_3(OH)$
Uptake of F^- (%)	89.9	68.5	21.0	21.0	97.8

Sample solution (sodium fluoride): $500\,\mu g\,F^-/50\,ml$, Calcium salt added: 0.5 g, Stirring time: 10 min

and the uptake efficiency increases in the following order: $NaF < NH_4HF_2 < HF$. The percent uptake of both hydrofluoric acid and ammonium hydrogen fluoride does not drop sharply and remains nearly constant even when the starting concentration gets higher as shown in Figure 3. The maximum capacity of hydroxyapatite from theoretical considerations is clearly exceeded in both cases; obviously fixation of fluoride ion proceeds by a different mechanism. A survey of literatures on hydroxyapatite showed that the complex binding mechanism such as matrix exchange and lattice inclusion had been also confirmed by evidence. These facts make the complete characterization of hydroxyapatite somewhat difficult. In Table II, result are presented for batch uptake of fluoride from aqueous solution using several kinds of calcium phosphate. The difference in percent uptake of fluoride is striking, with the best result for calcium hydroxyapatite.

Removal of fluoride by batch and column methods

As an application to environmental works, attempts are made for defluoridation of waste water collected from an electronics factory. The results are shown in Table III. It is possible to remove fluoride ions down to sub-ppm levels by a batch procedure. There was no limitation to this method in applying it to large-scale work in the laboratory.

One particularly attractive perspective is the eventual application of hydroxyapatite columns for continuous and on-line collection of fluoride from aqueous samples. The problem of the method is that the flow-rate of eluate changes remarkably during column operations. Increasing particle size showed little improvement in the elution characteristics. This difficulty is solved by encapsulating hydroxyapatite particles in organic structure, i.e. polyacrylamide resin. Typical retention characteristics for sodium fluoride and hydrofluoric acid are shown in Figure 4 and 5. The column

TABLE III

Removal of fluoride ion from waste water

Sample (ml)	pH of buffer added	H.A. added (g)	Residual F⁻ conc. (ppm)	Removal of F⁻ (%)
25	—	1.0	8.2	91.5
100	—	4.0	11.5	88.1
25	4	1.0	0.06	99.9
100	4	2.0	0.53	99.5
25	5	1.0	0.38	99.6
100	5	4.0	1.05	98.9

Initial concentration of waste water: 96.5 ppm F⁻ (pH 8.6)

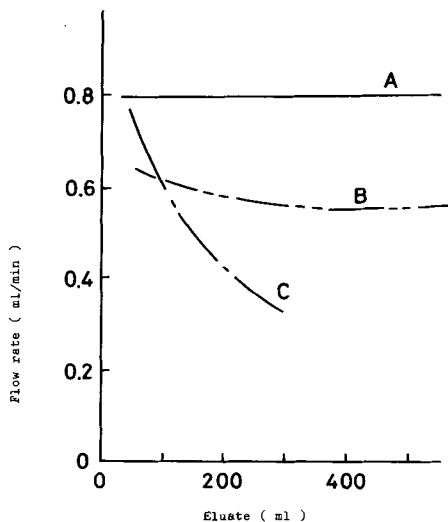ᵃAcetate buffer solution (0.1 M) was added to the sample with a ratio of 1:4.

FIGURE 4   Elution characteristics of hydroxyapatite column.
A:Modified hydroxyapatite (1.2 g)—HF solution (11.6 ppm F⁻).
B:Modified hydroxyapatite (1.3 g)—NaF solution (10 ppm F⁻, pH 3.3).
C:Hydroxyapatite (1.0 g)—NaF solution (10 ppm F⁻, pH 3.3).

method has successfully been applied to a hot spring water sample which contains 2.5 ppm of fluoride ion. Five hundred milliliters of sample solution was passed through a column and quantitative removal of fluoride was confirmed by the ion-selective electrode.

TABLE IV

Effect of Al^{3+} on F^- recovery

F^- taken (μg)	Al^{3+} present (mg)	F^- found[a] (μg)	Recovery (%)
50.0	2.5	50.0	100.0
	5.0	48.0	96.0
250.0	5.0	251.0	100.4
	12.5	251.5	100.6
	25.0	247.5	99.0
500.0	25.0	491.5	98.3
	50.0	509.0	101.8

Sample solution: 50 ml (0.05 M acetate buffer), H.A.: 1.0 g, Stirring time: 30 min.

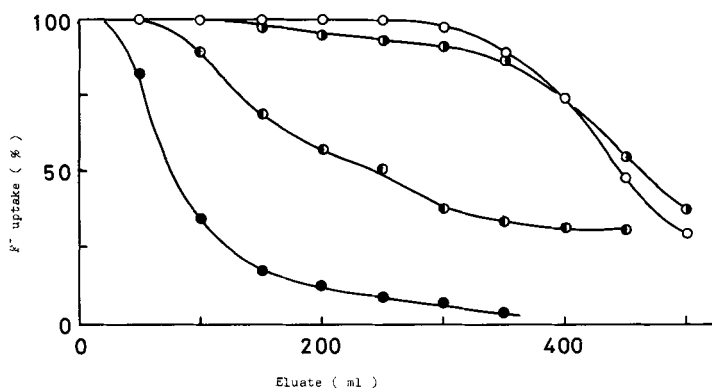[a]mean values of three experiments.

FIGURE 5 Uptake efficiency on hydroxyapatite column.
20 ppm F^- solutions are passed through the column (1.0 g of modified hydroxyapatite) at the flow-rate of 1.3 ml/min.
Sample solution:HF (O), NaF (pH 4.7, 0.05 M acetate) (◑), NaF (pH 4.0, 3×10^{-4} M HCl) (◐), NaF (no buffer) (●).

Application to fluoride determination

There are several applications where the usual method of fluoride measurement with a well-known ion-slective electrode fails. The most obvious example arises when the solution contains appreciable amounts of aluminium and other ions which complex with fluoride ions. The use of masking agents such as citrate[11] and Tiron[12] was reported, but their

ability depended strongly on ligand concentration and pH. A batch separation procedure is developed in which fluorides that are collected on hydroxyapatite are dissolved for potentiometric analysis. As shown in Table IV, fluoride ions $(50-500\,\mu g)$ are quantitatively recovered from a 100-fold excess of aluminium by 1 g of hydroxyapatite. Further analytical applications are in progress.

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