Extraction chromatographic method of preconcentration and separation of fluoride with high molecular mass liquid anion exchanger, Aliquat-336

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Abstract : A selective method has been developed for the extraction chromatographic separation of fluoride with Aliquat-336 (liquid cation exchanger) coated on silanised silica gel. Its quantitative extraction has been achieved in HCl medium at 0.1–0.3 M range. The effects of acid with different concentrations, flow-rate, stripping agents on extraction and elution have been investigated. Exchange capacity and break-through capacity of the prepared exchanger at different temperatures with respect to fluoride have been determined. The extraction equilibrium constant (K_{ex}) and different standard thermodynamic parameters have also been calculated by temperature variation method. Effect of influent concentration and influent volume on preconcentration factor (PF) has been investigated. Fluoride has been separated from synthetic binary and multi-component mixtures containing various anions associated with it in environmental samples. The method effectively permits sequential separation of fluoride from synthetic mixture containing its congeners, chloride, bromide and iodide of analytical group. The method was found effective for removal and recovery of fluoride from industrial waste and environmental samples following its preconcentration on the column. A plausible mechanism for the extraction of fluoride has been suggested.

Keywords : Aliquat-336, extraction chromatography, preconcentration, separation of fluoride, selective separation.

Introduction

Trace level separation of toxicant fluoride poses a challenging problem to the analytical chemists. The most widely used techniques for the separation and preconcentration of fluoride in trace level includes liquid-liquid extraction[1,2], co-precipitation[3], adsorption[4], ion-chromatography[5]. But these techniques may be ineffective or extremely expensive, when constituents are in large volumes of relatively low concentrations[6]. Extraction chromatography (EC) is now one of the most interesting areas in analytical chemistry for the trace level separation and preconcentration of constituents because it is simple, selective, rapid and cost effective[7-9]. Silica gel is found to act as a successful support since it does not swell or strain, has good mechanical strength and can undergo heat treatment[10]. EC is based on the utilization of a major constituent as the supporting phase with different coating materials[7-9] such as polyelectrolyte, high molecular mass carboxylic acid (HMMCA), chelating agent, surfactant, high molecular mass amine (HMMA) etc. The essential requirements of sorbents in EC are (i) the possibility to extract selectively a large number of analytes over a wide pH range, (ii) the quantitative sorption and elution ability, (iii) the kinetically faster sorption and desorption mechanism, (iv) the high retention capacity, (v) the regenerability, (vi) the accessibility and (vii) the mechanical and chemical stability[11]. Having these, quite a good deal of literature appears to deal with HMMCA and HMMA (Aliquat-336), on hydrophobic silica support for selective separation of metal ions[9,12-6]. But, systematic work on extraction chromatographic behavior of fluoride ion with these exchangers has yet not been reported. Aliquat-336 is an anion exchanger, soluble in several solvents like benzene, toluene, *n*-hexane, xylene, butanol, carbon tetrachloride, chloroform, nitrobenzene, and di-isopropyl ether[16]. It has a good thermal and chemical stability and efficiently extracted metal ions from aqueous solution over a wide range of acid strength[16]. The present work reports a rapid method for the extraction and preconcentration of microgram level fluoride with HMMA, Aliquat-336 on hydrophobic silica support.

Results and discussion

The systematic extraction chromatographic studies on fluoride with Aliquat-336 at the range 0.05–1.0 M HCl ensured its quantitative extraction at the range of 0.1–0.3 M HCl. The complete retention of fluoride at the column was found even at a flow rate of 2.5 mL min^{-1}. Systematic studies on the effect of a large number of foreign ions on the extraction of fluoride have been made. Common anions like Cl$^-$, SO$_4^{2-}$, ClO$_4^-$, PO$_4^{3-}$, NO$_3^-$ (up to 800, 200, 200, 700, 300 μg mL^{-1} respectively) and cations like K$^+$, Na$^+$, NH$_4^+$, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+} (up to 700, 800, 700, 200, 300, 500, 100, 100, 300, 300 μg mL^{-1} respectively) did not interfere in the quantitative (>97%) extraction (Table 1). At

not participate in the exchange process due to the backward reaction (eq. (1)) in increased concentration of Cl$^-$.

FTIR spectra of the exchanger in its chloride and fluoride form (i.e. after the extraction of fluoride) shows that there is no appreciable change in their spectral peak positions (Fig. 1). Here, the replacement of anions by one another on the identical R$_4$N$^+$ moiety occurred reversibly (eq. (1)).

The extraction equilibrium constant (K_{ex}) has been computed at different temperatures[17] using the following equation (eq. (2)) and the plot of log K_{ex} vs 1000/T gives a linear relationship ($y = -1.2018\ X + 4.5495$; $R^2 = 0.9988$).

$$K_{ex} = [Cl^-]\ E_R/[R_4N^+Cl^-] \qquad (2)$$

Table 1. Effect of interfering anions and cations on extraction of fluoride
Column = 0.8 × 8 cm^2; flow-rate = 2.0 mL min^{-1}; fluoride taken = 6 0 μg; HCl = 0.2 M

Interfering ion	Interfering ion conc. (μg mL^{-1})/Retention of fluoride (%)							
	100	200	300	400	500	600	700	800
Cl$^-$	99.2	98.6	98.4	98.2	98.1	97.7	97.6	97.4
SO$_4^{2-}$	98.6	98.1	88.3	86.2	85.2	78.0	75.5	74.6
ClO$_4^-$	99.1	98.7	96.3	88.4	85.9	81.5	78.9	76.9
NO$_3^-$	99.4	99.1	98.5	96.8	89.6	82.4	73.6	72.2
CH$_3$COO$^-$	99.7	99.6	99.2	98.5	98.0	97.4	95.4	92.3
PO$_4^{3-}$	99.7	99.7	98.6	98.3	97.8	97.6	97.4	95.7
K$^+$	99.9	99.8	99.6	99.4	99.1	98.8	97.8	96.2
Na$^+$	99.8	99.7	99.6	99.2	98.9	98.7	98.4	98.3
NH$_4^+$	99.9	99.4	98.8	98.2	97.9	96.4	96.0	95.3
Zn^{2+}	98.4	97.8	91.8	88.2	82.5	78.6	72.4	69 1
Cd^{2+}	98.3	98.1	97.6	95.4	94.1	91.6	88.7	87 8
Hg^{2+}	99.4	98.6	97.9	96.1	93.5	92.2	89.3	87.6
Pb^{2+}	98.1	97.3	95.2	86.2	74 1	68.1	44.0	22.6
Fe^{3+}	97.3	96.1	95.4	94.0	92.3	88.5	83.6	76.9
Ca^{2+}	99.2	98.4	97.8	94.1	88.4	76.9	59.3	36.0
Mg^{2+}	98.8	98.2	97.6	96.1	94.2	90.4	86.7	66.8

0.2 M HCl, plot of log D against log C [ex] gives a linear relationship with slope of 0.98 at fixed concentration of hydrochloric acid and fixed concentration of fluoride. Bearing this in mind it has been suggested that fluoride ion goes to the exchange site as per following proposed path :

R$_4$N$^+$Cl$^-$ (S) + Na$^+$F$^-$ (Sol.) $\rightleftharpoons$

R$_4$N$^+$F$^-$ (S) + Na$^+$Cl$^-$ (Sol.) (1)
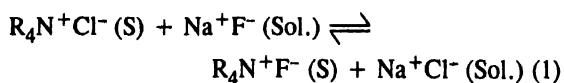
At higher concentration of HCl (>0.3 M), fluoride does

where, [R$_4$N$^+$Cl$^-$] denotes concentration of Aliquat-336 and E_R is the ratio of extracted fluoride ion to its unextracted portion.

The effect of temperature on extraction of fluoride has been made for the determination[17] of different thermodynamic parameters at pH 5.5 using the standard van't Hoff equation. The enthalpy change (ΔH) was evaluated from the plot of log K_{ex} vs 1000/T using equation (eq. (3)).
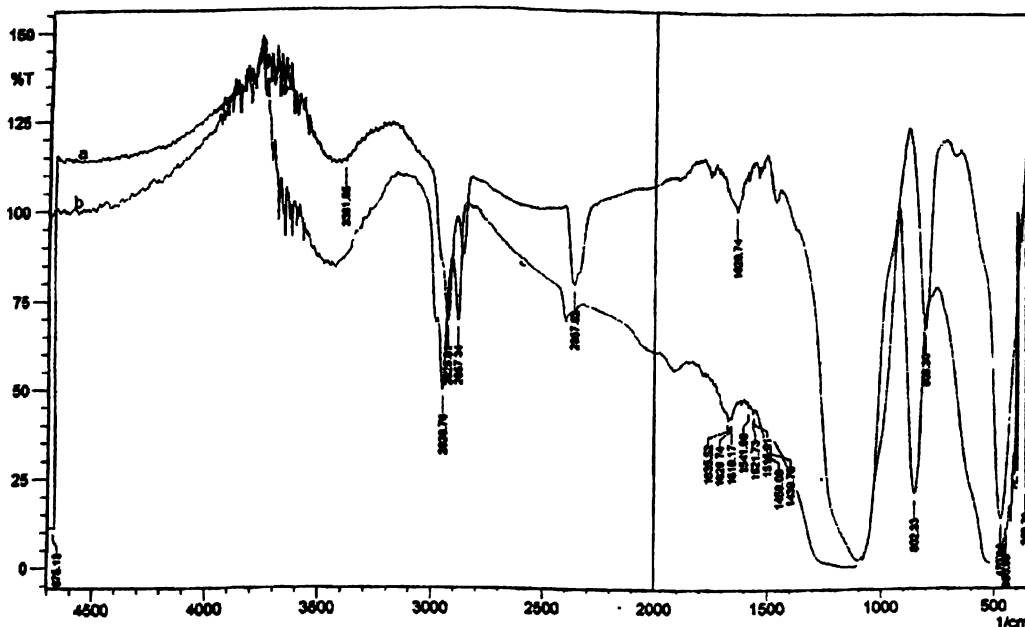
Fig. 1. (a) FTIR spectra of the exchanger in its chloride form, (b) FTIR spectra of the exchanger loaded with fluoride

$$(\Delta H) = -(\text{slope}) \times 2.303 \times R \qquad (3)$$

where, R is the gas consant $= 8.314$ J mol^{-1}.

The free energy change (ΔG) and entropy change (ΔS) at room temperature (298 K) were calculated using equations (eqs. (4) and (5)).

$$\Delta G = -2.303 \, RT \log K_{ex} \qquad (4)$$

and

$$\Delta S = (\Delta H - \Delta G)/T \qquad (5)$$

The positive value of ΔH (0.023 kJ mol^{-1}) and smaller ΔS (0.017 kJ mol^{-1}) rationalize the endothermic nature of the extraction process. The small negative value of ΔG (-5.2 kJ mol^{-1}) and low value of ΔH, indicate the spontaneity and reversible nature of the equilibrium (eq. (1)) and agreed well with the FTIR analysis.

After extraction, to select the specific stripping agents, fluoride was stripped with demineralised water and hydrochloric acid of different concentrations. The systematic studies on stripping behavior gave the quantitative elution of fluoride with HCl at the concentration ≥ 2 M.

The systematic extraction chromatographic studies on fluoride of concentration range 10–13 μg mL^{-1} with HMMA, Aliquat-336 at the range of 0.2–0.3 M HCl shows

(Table 2) that the preconcentration factor (PF) has been increased with increase in volume of the influent as expected. Also the PF at a constant volume of influent turns out to be independent of variation in acid concentration and influent concentration. However, the result shows that up to an influent volume of 600 mL, recovery of fluoride becomes quantitative (>97%) with PF ~58.3. To reach the breakthrough values 7500 μg (at 0.3 M HCl) and 8400 μg (at 0.2 M HCl), respectively 750 mL of 10 μg mL^{-1} and 700 mL of 12 μg mL^{-1} of sample were passed, when the recoveries were found to be poor. Thus, PF did not attain its maximum possible values 75 and 70 at 0.3 M HCl and at 0.2 M HCl respectively as the recoveries were less than 100%. However, PF has been optimized at about 63.3 $\pm$ 0.1.

Ion-exchange paper chromtography : The R_f values was determined in acetatic acid : hydrochloric acid (1 M) : acetone (1 : 1 : 4 v/v) on chromatogram (Table 3). Result shows that under this recommended condition bromide is very weakly bound, iodide is moderately bound while fluoride is very tightly bound with the stationary phase. Bromide, fluoride and iodide were detected by spot reagents[18].

Table 2. Effect of HCl concentration and volume on preconcentration factor
Amount of exchanger = 1 g; stripping agent = 10 mL 2 M HCl

HCl conc. of the sample	Sample conc. (C_s) (μg mL^{-1})	Sample volume, V_s (mL)	Amount of F$^-$ (μg)		Effluent conc. (C_f) (μg mL^{-1})	Recovery[a] (%)	PF (C_f/C_s)
			Added	Recovered			
0.3 M	10	400	4000	3968	397	99.2	39 7
		450	4500	4441	444	98.7	44.4
		500	5000	4890	489	97 8	48 9
		550	5500	5368	537	97.6	53.7
		600	6000	5832	583	97.2	58.3
		650	6500	6227	623	95.8	62.3
		700	7000	6307	631	90.1	63.1
		750	7500	6315	632	84.2	63.2
0.2 M	12	400	4800	4742	474	98.8	39.5
		450	5400	5319	532	98.5	44.2
		500	6000	5886	589	98.1	49.1
		550	6600	6455	645 ·	97.8	53.8
		600	7200	7006	701	97.3	58.4
		650	7800	7456	746	95.6	62.2
		700	8400	7610	765	90.6	63.4

[a]Average of five determination; PF = ratio of effluent concentration to sample concentration (C_f/C_s).

Table 3. R_f values of different anions on Whatman No. 1 impregnated with Aliquat-336
Time = 2.5 h; developing solvent = acetatic acid : hydrochloric acid (1 M) : acetone (1 : 1 : 4 v/v)

Anions	Solute front (cm)	Solvent front (cm)	R_f values	Affinity order (increasing)
Iodide	13.6	14.6	0.93	I$^-$
Bromide	6.8		0.46	Br$^-$
Fluoride	1.2		0.08	F$^-$

Separation of fluoride from binary mixtures : Fluoride was separated from several anions in binary mixtures. The binary mixtures were prepared by mixing an aliquot of standard solution containing 6 μg of fluoride and one of other anions in 12–15 mL 0.2 M HCl. The separations were achieved either by exploiting the difference in concentration of hydrochloric for extraction or by using suitable selective eluents. Binary mixtures containing fluo-

Table 4. Important binary and ternary separations of fluoride
Flow-rate = 1.0 ml min^{-1}; HCl = 0.2 M; fluoride = 6.0 μg

Anions	Wt. of the anions (μg)		Recovery (%)	Accuracy (%)	Eluent used	Eluent vol. (mL)
	Added	Recovered				
F$^-$	6.0	5.92	98.6	−1.33	2 M HCl	10
SO$_4^{2-}$	30.20	30.44	100.8	+0.79		20
F$^-$	6.0	5.90	98.3	−1.66	2 M HCl	10
NO$_3^-$	10.35	10.42	100.7	+0.67		20
F$^-$	6.0	6.05	100.8	+0.83	2 M HCl	10
I$^-$	2.74	2.68	97.8	−2.18	1 M HCl	20
F$^-$	6.0	5.94	99.0	−1.0	2 M HCl	10
Br$^-$	3.20	3.26	101.9	+1.87	0.5 M HCl	20
F$^-$	6.0	5.88	98.5	−1.45	2 M HCl	10
PO$_4^{3-}$	6.62	6.74	101.8	+1.81		20
F$^-$	6.0	6.12	102.0	+2.0	2 M HCl	10
Br$^-$	3.20	3.13	97.8	−2.18	0.5 M HCl	20
I$^-$	2.74	2.79	101.8	+1.82	1 M HCl	20

Average of five determinations : standard deviation <0.07.

ride with sulfate, perchlorate, phosphate and nitrate when equilibrated with the exchanger at 0.2 M HCl, the diverse ions passed through the column with the mobile phase. Under this condition only fluoride was extracted at the column and was eluted with 2 M HCl. However, at 0.2 M HCl from the binary mixtures the diverse ions like bromide and iodide were extracted along with fluoride. From the respective mixtures of fluoride-bromide and fluoride-iodide, selectively bromide and iodide were eluted first with 0.5 M HCl and 1 M HCl. Then fluoride was eluted with 2 M HCl. Sequential separation of fluoride, bromide and iodide has been achieved by passing the mixture containing all the anions at 0.2 M HCl. Under this condition all the anions were extracted at the column. Bromide was first eluted with 0.5 M HCl, followed by the elution of iodide and fluoride has been made with 1 M HCl and 2 M HCl respectively. All the anions were determined spectrophotometrically[19]. The method is quite reproducible with low standard deviation (>0.08) and to ensure adequate precision, average values of three independent determinations were taken for each anion. The recovered amount was compared with the known amount of added metal ions and the accuracy was found to be within ±2%. Results are given in Table 4.

High degree of preconcentration (600 ml to 10 ml) (PF = 58.5 ± 0.3) with subsequent removal, or recovery ($>97\%$) of fluoride with low standard deviation (<0.38) have been reached (Table 5). Probably, entrapped water, leach and dissolve locally concentrated pockets of highly soluble villiaumite (NaF) within volcanic trap rock during its journey from a secondary aquifer to the surface[20]. Amount of fluoride in real samples have been determined by ion selective electrode.

Experimental

Apparatus : Digital Elico Ll-120 pH meter combined with glass electrode, a 7D-1F thermostat, spectrophotometer (Beckman DU-6 ECIL GS 5700A), Thermo Scientific (Orion 5 Star Benchtop Multi W/ISE mtr, Singapore), chromatographic glass column (0.8 × 8 cm) with glasswool plug at the bottom was used in the present study.

Reagents : The anion exchanger, Aliquat-336 (Fluka-AG) a high molecular mass synthetic quaternary ammonium compound (tricapryl-methyl ammonium chloride) was used. Dimethyldichlorosilane was used to make the silica gel (120 mesh) hydrophobic. A standard stock solution of fluoride (6 μg mL^{-1}) was prepared by dissolving NaF (A.R.) in water and estimated spectrophoto-

Table 5. Preconcentration and recovery of fluoride
Column = 0.8 × 8 cm^2; flow-rate = 1.0 mL min^{-1}; pH = 5.0; Temp. = 25 °C

Sample no.	Fluoride solution passed (mL)	Initial concentration of fluoride in the influent, C_i (mg/mL)	Eluent used (2 M HCl) (mL)	Concentration of fluoride in the effluent, C_e (mg/mL)	Recovery (%)	PF (C_e/C_i)
1D	600	0.006	10	0.349	97.0	58.2
2D	600	0.01	10	0.584	97.3	58.4
1T	600	0.14	10	8.18	97.5	58.4
2T	600	0.27	10	15.89	98.1	58.8
3T	600	0.23	10	13.52	98.0	58.8

Effectiveness and utility of the proposed method : The feasibility of the process was tested with the real samples obtained from five different places of Nalhati block in Birbhum district, West Bengal. Geologically, the area (24°32′ 30″N–24°35″N and 87°01″–87°05′2″E) consists of fine grained, hard, and compact basaltic rocks. These rocks posses negligible primary porosity but acquire secondary porosity by fracturing and weathering. The topography is moderately hilly with very sparse vegetation.

metrically[19]. All of these chemicals and solvents used in this work, unless otherwise stated, were of analytical grade (BDH/E. Merck).

Preparation of ion exchange material : Silica gel (120 mesh) was rendered hydrophobic by exposing it to the vapor of dimethyldichlorosilane (DMDCS) in N$_2$ atmosphere. The DMDCS treated (silanised) silica gel was then washed with anhydrous methanol and dried at 100 °C. The silanised silica gel was impregnated with Aliquat-

36, diluted in benzene and was dried in a rotary vacuum evaporator to achieve uniform coating[21]. Excess benzene was removed by washing the exchanger with 2 M HCl. Each column could be used for at least 30 cycles without any loss of its exchange capacity. For ion-exchange paper chromatography, 0.5 ml Aliquat-336 was taken in 20 ml benzene and paper strip (Whatman No. 1) was immersed in it and dried in air. Microgram level fluoride solution was taken on the paper strip containing exchanger and developed with acetatic acid : hydrochloric acid (1 M) : acetone (1 : 1 : 4 v/v) as the developing solvent.

Exchange capacity and break through capacity of the prepared exchanger : The exchange capacity of the prepared exchanger was determined[16] at different temperatures by measuring the milligram equivalent of OH^- ions absorbed by 1 g of dry exchanger in chloride form. The liberated chloride ion was titrated against standard $AgNO_3$ solution using potassium chromate indicator. The exchange capacity of the prepared exchanger was found to be 0.58 meq. Cl^-/g at 30 °C. 1 g of dry exchanger was taken in the column and at 0.2 M and 0.3 M HCl medium 20 μg mL^{-1} fluoride solution was passed through the column at a flow-rate of 2 mL min^{-1}. It was found that the leakage of fluoride started after passing 375 mL (7500 μg) and 420 mL (8400 μg) of effluent at 0.3 M and 0.2 M HCl respectively. After its extraction fluoride was eluted with 10 mL 2 M HCl. So the method magnifies the concentration of fluoride (840 μg mL^{-1}) in the effluent with a preconcentration factor (PF) of 42 at 0.2 M HCl condition.

General extraction procedure : 3 g of Aliquat-336 impregnated with silica gel, was slurred with deionised water and was loaded in a chromatographic column (0.8 × 6.5 cm). The column was washed with 2 M HCl followed by deionised water. 20 ml 0.2 M HCl was passed through the column. An aliquot containing 6 μg of fluoride in 0.2 M HCl was passed through the column (pre-adjusted at 0.2 M HCl), at a flow rate of 2.0 min^{-1}. After extraction fluoride was stripped with 2 M HCl. A number of fractions were collected and the amount of fluoride from each fraction was determined spectrophotometrically[19] using sodium 2-(parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfonate (SPADNS) reagent at 570 nm.

Conclusion :

The proposed method is simple, rapid and selective and need only 2.5 h for complete work involving separation and estimation of fluoride. The method was found selective at the optimized conditions for the separation of fluoride and does not need the separation of other constituents like K^+, Na^+, NH_4^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, ClO_4^-, PO_4^{3-}, NO_3^-, present in the matrix (Table 1). The developed exchanger is chemically stable (up to 6 M HNO_3, 4 M CH_3COOH, 4 M HCl and 2 M H_2SO_4), effective over a wide range of pH and can be used for more than 30–40 cycles without any loss its exchange capacity[16]. These show its additional advantages over the other conventional exchangers[21]. Results achieved in all this experiments are satisfactory, recoveries were quantitative ($>97\%$), standard deviation was <0.07 and the relative error was within $\pm2.3(\%)$.

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