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Use of Some Transition Metal Cations in Potentiometric and Spectrophotometric Microdetermination of Fluoride and Evaluation of its Uptake Rate by Tooth Enamal

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In this work silver amalgam electrode was utilized for potentiometric microdetermination of fluoride (50–1500 ppm) and its uptake rate (6.5 to 14.9 mg.) by tooth enamel powder (1 gm) under various conditions. The determination depends upon the mercurimetric titration of excess EDTA added to excess of metal cations as Fe (III), Th (IV) and Sm (III) that remained after interaction with fluoride sample. This work was successfully applied in spectrophotometric microdetermination of fluoride (13–380 ppm) and its uptake by tooth enamel powder (25.5 to 179 mg/1gm) via fading of colour of Fe (III)–thiocyanate and Fe (III)-salicylate complexes. This work proved that the fluoride used in tooth remedy is mostly chemically bonded to the tooth construction but that physically absorbed was washed with water. It was observed that as the concentration of fluoride and the time of contact with tooth enamel were increased the fluride uptake rate by the enamel powder increased.

INTRODUCTION

The analysis of fluorine-containing materials had attracted the interest of scientist. The reason for this was not only to the widespread interest in the fluoride content of water, air, biological materials and insecticides, but also to the characteristic features of fluorine chemistry which makes its analysis difficult[1]. During the recent years, trace amounts of fluoride have been determined most commonly by the photometric[2], a fluoride ion-selective electrodes[3–10], enzyme-catalyzed reaction[11], photokinetic[12] and spectrophotometric methods[13–15] Human demineralized enamel samples were analyzed by a microdrill method[16]. The total fluoride was determined in toothpastes[17]. Also, fluoride was determined in several plant samples by a potentiometric method and near-infrared reflectance spectroscopy[18].

This work describes both potentiometric and spectrophotometric as rapid and

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simple methods for microdetermination of fluoride in aqueous media. Because of the public health significance of aqueous fluoride solution used for tooth remedy, the determination of fluoride uptake rate by tooth enamel becomes extremely important, which is the ultimate object of this work.

EXPERIMENTAL

All the chemical were of the reagent grade. They included EDTA, eriochrome black T(EBT) and methylxymol blue indicators, hexamine, zinc oxide, ammonium chloride and hydroxide, thorium nitrate, ferric sulphate, salicylic acid, mercuric nitrate, sodium and potassium fluoride, samarium perchlorate, sodium hydroxide, potassium thiocyanate (all from BDH) and enamel powder. Deionized water was also used. The titration cell and potentiometer were described elsewhere[19]. The spectrophotometric measurements were performed using a Perkin-Elmer Lambda 1C 632–0001 Spectrophotometer.

0.05 M standard zinc solution was used for standardization of 0.05 M stock solution of EDTA using EBT indicator[20] in ammoniacal buffer of pH 10. The standard 0.0463–0.0562 M EDTA solutions were used for standardization of metal ions solutions potentiometrically in hexamine buffer media and visually using recommended procedures[19-22]. The standardized stock solutions of 0.0655 M Fe (III), 0.041–0.044 M Hg (II), 0.01–0.0139 M Sm (III), 0.047–0.0442 M Th (IV), 0.2 M NaOH and 10% hexamine were used. The diluted solutions of 0.01 to 10^{-3} M of these metal cations were used in spectral measurements. The 1–2% and 0.3–5 M stock solutions of fluoride ions were used in this work. The 2 M thiocyanate solution was used to form the blood red coloured hexathiocyanatoferrate (III). Complex anion, which together with a 0.0566 M violet salicylatoferrate (III) chelate were used for spectrophotometric determination of fluoride.

Procedures

(1) Potentiometric Procedures

(a) *Potentiomercurimetric Microdetermination of Fluoride*: It involves addition of known volumes of standard metal cations solutions as Fe (III), Th (IV) or Sm (III) to fluoride solutions with different concentrations in a titration tiflon 100 ml vessel during constant stirring for 5 minutes; followed by the addition of excess standard EDTA and completing to a constant volume by 10% hexamine buffer of pH 8–10. The unconsumed EDTA was then back titrated against Hg (II) using silver amalgam electrode and SCE combination. EDTA consumed= unconsumed metal cations, from which the fluoride concentration can easily estimated (Table 1).

TABLE 1
POTENTIOMETRIC MICRODETERMINATION OF FLUORIDE VIA INTERACTION WITH SOME TRANSITION METAL CATIONS M = Fe (III), Th (IV) AND Sm (III) USING SILVER AMALGAM ELECTRODE.

M	fluoride (ppm)		% Recovery	Potential break/ 0.1 ml Hg (II)
	Taken	Found		
Fe (III)	1050	1048	99.8	95
	990	997	100.7	95
	740	748	100.1	100
	500	520	104.0	120
	400	412	103.0	200
	300	312	104.0	228
	50	52	104.5	300
Th (IV)	1010	1014	100.5	200
	950	955	100.5	215
	800	810	101.2	230
	600	615	102.5	250
	500	530	106.0	300
	100	106.5	106.5	320
	50	53	106.5	340
Sm (III)	1500	1520	101.3	275
	1000	988	98.8	295
	800	810	101.2	300
	700	712	101.7	305
	570	572	100.5	320
	100	101	101.0	340
	50	51	102.0	350

(b) *Potentiometric Determination of Fluoride Uptake rate by Tooth Enamel:* It involves addition of different excess known volumes of standard fluoride to a series of 0.2 gm enamel powder, which kept in a tiflon beaker, leaving them together for different time intervals (from 2 to 20 min). Each sample was filtered and the enamel washed several times with equiportions of deionized water. The filterate was transferred into a 100 ml measuring flask and completed with deionized water up to the mark. 10 to 20 ml of the filtrate was transfered to a titration vessel and the remaining fluoride was determined potentiometrically by applying the procedure (A). The uptake fluoride rate was calculated by difference between added fluoride to enamel and the remaining one (Table 2).

TABLE 2
POTENTIOMETRIC MICRODETERMINATION OF FLUORIDE UPTAKE BY ONE GRAM TOOTH ENAMEL POWDER VIA INTERACTION OF REMAINDER FLUORIDE WITH Sm (III) and Th (IV)

Metal ion	Sample No.	Flouride (ppm)		Fluoride uptake by 1 gm enamel		Time of contact
		Added to 1 gm enamel	Remained	ppm	%	
Sm (III)	1	136.0	129.5	6.5	4.8	2
	2	263.0	139.0	124.0	47.1	4
	3	441.0	369.0	42.0	10.2	12
Th (IV)	4	224.5	45.5	179.0	88.6	4
	5	224.5	145.5	79.0	35.2	10
	6	224.5	159.0	65.5	29.2	15
	7	224.5	184.0	40.5	18.0	20

The mercurimetric determination of fluoride by potential measurements depends mainly upon the fact that Fe (III), Th (IV) and Sm (III) form fluorides of conditional formation constants $K_{MF} > K_{M\text{ - EDTA complexes}} > K_{Hg\text{ - EDTA}}$ under the given experimental condtions[23]

(2) Spectrophotometric Procedure

It involves two steps

(a) The preparation of the coloured iron-thiocyanate complex and iron-salicylate chelate and the calibration curve by addition of different known concentration of very dilute (0.01 to 0.001 M) fluoride to a known excess coloured complex in 25 ml measuring flask and plot of absorbance values against fluoride concentration. The absorbance of the complex was decreased with the increase of fluoride concentration. This is due to the fact that iron forms a stable compound than its complex with thiocyanate or salicylate anions[23]. The concentration of the unknown fluoride (Table 3) can be obtained directly from the calibration curve.

(b) The microdetermination of the fluoride uptake by tooth enamel was determined by dilution of filtrate of the procedure (1 b) to 250 ml. The remaining fluoride was determined by addition of a very small volume of the fluoride filtrate (0.05 ml – 5 ml) to 1–2 ml of the coloured complex. The absorbance values of the remained complex was measured at λ_{max} of 490 and 527 nm for Fe-thiocyanate and Fe-salicylate respectively. From these absorbance values, the remaining fluoride was determined from the calibration curve. The fluoride uptake rate by 0.2 gm was determined and by 1 gm tooth enamel was then calculated as shown in procedure (1 b) (Table 4).

TABLE 3
SPECTROPHOTOMETRIC MICRODETERMINATION OF FLUORIDE BY INTERACTION WITH Fe (III) COLOURED COMPLEXES OF (a) SALICYLATE AND (b) THIOCYANATE LIGANDS.

(a)			(b)		
Fluoride (ppm)		% Recovery	Fluoride (ppm)		% Recovery
Taken	Found		Taken	Found	
24.7	24.5	99.8	13.3	12.56	94.4
49.4	48.0	97.0	26.6	28.5	105.18
74.1	79.0	106.0	53.2	54.88	103.15
98.8	104.0	105.0	79.8	81.3	101.87
123.5	122.3	99.5	106.4	102.0	95.77
148.2	148.2	100.0	133.0	117.0	87.96
172.9	167.7	96.5	159.6	137.0	85.83
197.0	177.9	90.0	186.2	154.0	82.70
222.3	187.0	84.0	212.8	165.0	77.53
296.0	205.0	69.0	239.0	176.0	73.64

TABLE 4
SPECTROPHOTOMETRIC MICRODETERMINATION OF FLUORIDE UPTAKE BY ONE GRAM TOOTH ENAMEL POWDER WITHIN 4 MIN. DEPENDING UPON ITS INTERACTION WITH (a) Fe (III)–SALICYLATE (b) Fe (III) THIOCYANATE INDICATORS

	Sample No.	Fluoride (mg)		Fluoride uptake by 1 gm enamel	
		Added	Remained	mg	%
(a)	1	47.5	22.0	25.5	53.7
	2	95.0	39.0	56.0	58.9
	3	142.5	43.5	99.0	69.5
	4	190.0	44.1	145.9	76.8
	5	237.5	44.6	192.9	81.2
	6	283.0	139.0	144.0	50.9
(b)	1	47.5	12.1	35.4	74.5
	2	95.0	17.9	77.1	81.1

RESULTS AND DISCUSSION

Potentiometric Microdetermination of Fluoride

The results from microdetermination of fluoride, by mercuripotentiometric technique utilizing the silver amalgam as an indicator electrode are shown in Table-1. The percentage recovery of 50–1050, 50–1010 and 50–1500 ppm fluoride are ranged 104 to 99.8, 106 to 100.5 and 102.0 to 98.8%, by using Fe (III),

Th (IV) and Sm (III) metal cations respectively. This indicates that, the percentage recovery of fluoride always increases with the decrease of its concentration on using Fe (III) and Th (IV), but it is approximately constant on using Sm (III); consequently the use of Sm (III) in potentiometric microdetermination of fluoride is more preferable than the other two metal cations. Therefore, percentage recovery, standard deviation (SD) and coefficient of variation (CV) for microdetermination of 500 ppm fluoride for 8 replicates are determined using Sm (III), which are found to be 99.6 to 101.7%, 0.756 and 0.135 respectively. These values are refer to the high accuracy, precision and reliability of the given procedure in case of using Sm (III). Sharp potential breaks were obtained at the end points ranged from 95 to 300,200 to 340,275 to 350 mV/0.1 ml Hg (II) in case of using Fe (III), Th (IV) and Sm (III) respectively. The reproducibility of these results and the high potential breaks obtained on using Th (IV) and Sm (III), are encouraged the use of this procedure in microdetermination of fluoride and its uptake rate by tooth enamel.

Potentiometric Microdetermination of Fluoride Uptake by Tooth Enamel

Table-2 shows the potentiometrically determined fluoride uptake by tooth enamel expressed in mg F^- per one gram enamel powder. These results show that, the taken amount of F^- by one gram enamel is maximum at 4 min. as indicated by the high percent of F^- consumed in tooth remedy. The per cent is usually decreased by the increase of time of contact between fluoride and enamel; which may be attributed to the following equilibrium,

$$\underset{\substack{\text{enamel hypothetical}\\ \text{form}}}{R\text{–}Ca(OH)_2} + 2F^- \rightleftharpoons R\text{–}Ca(F)_2 + 2OH^-$$

This means that there is an equilibrium between the reacted and the liberated F^- which only may attain after 4 min. It is also indicates that, the pH of seliva of the mouth together with the concentration of F^- are the main factors controlling this equilibrium. Since the washing of enamel several times with deionized water eliminates no F^- from its moiety. This means that fluoride is chemically bonded. The treatment of enamel with constant amount of fluoride (44.7 mg or 2%, NaF) at different time intervals, the uptake of fluoride, determined via interaction with Th (IV), decreased by the increase of time after 4 min. This clarify the use of 2% NaF aqueous solution by the predental physicians as a tooth remedy for 4 min. several portions.

Spectrophotometric Microdetermination of Fluoride and Its Uptake by Tooth Enamel

In order to confirm the above results two spectrophotometric reagents Fe (III)-thiocyanate and Fe(III)-salicylate complexes are used. This work depends on the fading of colour of these complexes on addition of fluoride, which is linearly related to the fluoride concentration. The obtained results are shown in

Tables-3 and 4. In Table-3 the percentage recovery values (99.8 to 100%) of fluoride indicate that iron-salicylate indicator can be used for the more accurate determination of F^- only in the concentration range 25 to 148 ppm and iron-thiocyanate can be used for the concentration range 26.6 to 106.4 ppm (recovery per cent 95.77 to 105 %).

Table-4 shows that, the uptake (mg) by one gm. of tooth enamel is spectrophotometrically followed by both Fe (III)-salicylate, which is more sensitive, and Fe (III) thiocynate which is less sensitive. Five samples (47.5 to 283 mg F^-/1 gm enamel) were analyzed by the first indicator and two other samples (47.5 to 95 mg/1 gm enamel) were performed by the second indicator. These results were obtained by addition of fluoride to tooth enamel powder followed by filtration and washing. The fluoride in filtrate was determined as given by procedure 2.

The uptake of F^- within 4 min. by one gm. tooth enamel powder is spectrophotometrically tested using both indicators to determine fluoride in the concentration range 47.5 to 383.0 mg. The obtained data refer to the increase of the uptake of F^- (53.7 to 81.2%) with the increase of fluoride concentration added (95 to 237.5 mg) due to the shift of the above equilibrium to the forward direction; but the remainder F^- is approximately constant (43.5 to 44.6 mg/ 1gm enamel). When the fluoride concentration added exceeded 283 mg the uptake per cent decreased from 81.2 to 50.9%; which may be attributed to the repelling forces of the physically adsorbed fluoride layers by the chemically bonded one.

Conclusion

It is finally concluded that the fluoride can efficiently determined potentiometrically by silver amalgam electrode via formation of insoluble fluorides with Fe (III), Sm (III) and Th (IV) and spectropohtometrically via its interaction with Fe (III)-salicylate and Fe (III)-thiocyanate through the fading of their colours. It is also concluded that the fluoride uptake by tooth enamel is achieved by chemical bonding to tooth construction followed by physical adsorption in excess F^-. This uptake increases with increase of F^- to certain concentration and decreased which explained by formations of monochemical layer and repulsion of excess physically absorbed layers. The uptake is also increased with time 4 min. at constant F^- concentration and it decreased at higher time due to the repulsion of physically absorbed layers.

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