Indirect voltammetric detection of fluoride ions in toothpaste on a comb-shaped interdigitated microelectrode array

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ABSTRACT

A novel technique based on dynamic electrochemistry for the detection of fluoride ions was developed. It is based on its strong complexation with ferric ion. Formed fluoroferric complex is cathodically inactive at the potential of the reduction of free ferric aquo ion. The voltammetric and amperometric response of platinum comb-shaped interdigitated microelectrode array is decreased after fluoride addition. This decrease serves for the quantification of fluoride ions added to the solution. The detection limit of 4.5×10^{-5} mol dm^{-3} was achieved when one of the segments of interdigitated microelectrode array (IDA) was used as an indicating electrode. The detection limit is about one order of magnitude lower than in the case of conventional platinum macroelectrode. In comparison with ISE electrodes this method is faster and also avoiding large error resulting from the antilogarithmization of ISE Nerstian response. The method was applied to the analysis of toothpaste.

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1. Introduction

Simple anions or their derivatives play an important role in biological, chemical and technological processes, therefore there is an increasing interest in the development of analytical methods for their detection. Fluoride anion is a relevant species in toothpaste for caries prevention. Its quantification, however, is limited to a few methods.

The most popular in this respect is fluoride ion selective electrode (ISE) introduced by Frant and Ross [1]. This device has a membrane with single crystal of LaF$_3$ with high electrical conductance, good mechanical properties, wide fluoride concentration range response as well as an enhanced selectivity for fluoride ion [2]. This approach was used for fluoride detection in waters [3], wines [4] and teas [5]. The response of ISE is Nernstian what may cause a large error of analytical results due to necessity of antilogarithmization. It also needs long times for signal obtaining because it takes a time for equilibrium establishment. This problem is partially solved in flow solution when tubular fluoride potentiometric electrode with a single LaF$_3$ crystal is used in FIA analysis [6].

Other methods recently published are based on ion-pairing chromatography [7], fluorescence [8] and colorimetry [9].

Microstructures with interacting diffusion layers [10] and interdigitated microelectrode arrays [11] are very popular in contemporary electrochemistry. They can be used as HPLC [12], biamperometric [13] or FIA [14] detectors in various applications as well as for mechanistic studies in reaction electroanalysis [15].

In this paper a method for the detection of fluoride ions based on dynamic electrochemistry is presented. It is based on chemical reaction of fluoride with ferric ion forming fluoroferric complex which is electroinactive at the potential of the reduction of ferric aquo ion. A conventional interdigitated microelectrode array [16] with interconnected segments is used as an amperometric detector of unreacted ferric ion. In this study we would like to extend the amperometric approach of IDA towards electroinactive species with limitations of dynamic electrochemical detection.

2. Experimental

A commercially available double comb-shaped planar interdigitated platinum microelectrode array from ALS Company, Tokyo, Japan (Fig. 1) was used. The device was formed on thermally oxidized silicon wafer. The widths of both microelectrode digits and the gap between them were 5 μm. The whole system had 65 2-mm long digits.

Model PAR 273A potentiostat (EG&G, Princeton Applied Research, Princeton, NJ) was used for electrochemical measurements. The reference electrode was conventional SCE and platinum macroelectrode of area 1 cm^2 served as a counter.

* Corresponding author at: Institute of Analytical Chemistry, Slovak University of Technology, Radlinského 9, Bratislava, SK-812 37, Slovak Republic. Fax: +421 2 59325590.
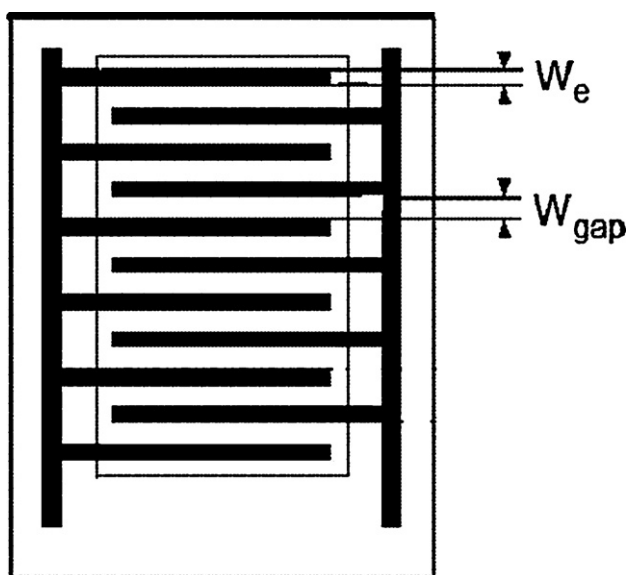*E-mail address:* peter.tomcik@ku.sk (P. Tomčík).

Fig. 1. A schematic depiction of commercial Pt IDA microelectrode ALS Co., Ltd., Tokyo, Japan. Width of digit W_e and gap W_{gap} are 5 μm, length of digit is 2 mm, number of digits in both arrays is 65, thickness of Pt film is 1 μm. The whole electrode is covered with non-conductive insulating film except active window area of 2×4 mm (depicted as a frame).

Fig. 2. Linear sweep voltammograms of 2×10^{-3} mol dm^{-3} Fe^{3+} in 0.2 mol dm^{-3} NaCl; scan rate 50 mV/s for curve 1, 100 mV/s for curve 2, 200 mV/s for curve 3.

19 mL of 0.2 mol dm^{-3} sodium chloride (NaCl, Lachema CZ) as a supporting electrolyte and 1 mL of 0.04 mol dm^{-3} ferric chloride (FeCl$_3$, Lachema CZ) was pipetted into an electrolytic cell. Additions of 0.25 mol dm^{-3} sodium fluoride (NaF, Lachema CZ) were pipetted. Fluoride stock solution was stored in polyethylene flask to avoid interferences by Si(IV), which forms complex with fluoride ion and reduces the free fluoride concentration in the stock solution.

Toothpaste from several suppliers served as real sample. Approximately 1 g of the sample was weighed into a 100 mL teflon beaker containing 30 mL of water. The mixture was boiled for 5 min to allow total dissolution of the suspension. Then it was infused to column filled with ion exchanger Dowex X-4 in H$^+$ cycle to bond some cations (e.g. Al^{3+}) forming complexes with fluoride to avoid possible interference or decreasing free fluoride amount in the sample. Finally, the eluent was transferred into 50 mL polyethylene volumetric flask with 0.5 mL of 0.04 mol dm^{-3} FeCl$_3$ and filled at the mark with 0.2 mol dm^{-3} NaCl. All chemicals were of analytical grade purity and triply distilled water was used for the preparation of all solutions.

3. Results and discussion

First, an optimization experiment was performed. It was observed that the pH value influences reduction current of Fe(III). When pH is decreased cathodic current increases. However, solutions with very low pH values (less than 2) may damage a chip with interdigitated microelectrode array. In addition, fluoride complexation with Fe(III) is negatively influenced what causes decrease of current difference after fluoride addition in strongly acidic media. At higher pH values (above 8) reduction current of free iron(III) decreases and it fully disappears in weakly alkaline solutions. pH value of 5–7 appears to be optimal and is in a close agreement with previous studies [17]. This pH interval also coincides with pH values of toothpaste solutions prepared by the above-described procedure. Moreover current does not depend upon NaCl concentration (0.1–1.0 mol dm^{-3}) in this pH interval. Therefore and due to its simplicity 0.2 mol dm^{-3} NaCl was chosen as a supporting electrolyte.

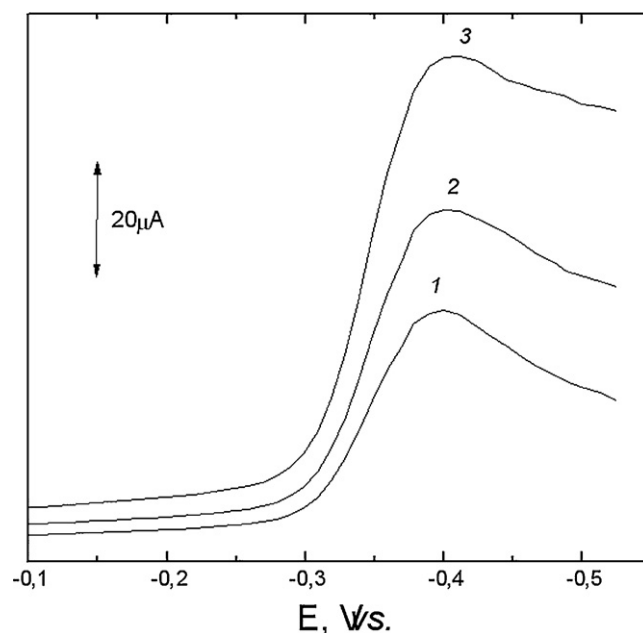Secondly, the charge transfer of iron(III) on platinum interdigitated array (IDA) was studied by linear sweep and cyclic voltammetry. Dependence of linear sweep voltammetric reduction response of 2×10^{-3} mol dm^{-3} FeCl$_3$ solution in 0.2 mol dm^{-3} NaCl on scan rate (50, 100 and 200 mV.s^{-1}) in the potential range from 0 V to -0.5 V vs. SCE was measured (Fig. 2.). Slight shift of cathodic peak potential dependent on scan rate towards the negative potential was observed. Cyclic voltammograms (Fig. 3) of 2×10^{-3} mol dm^{-3} FeCl$_3$ solution in 0.2 mol dm^{-3} NaCl were scanned from 0 V to -0.7 V vs. SCE and back with a scan rate of 50 mV s^{-1}. At the potential of about -0.4 V a large very well-developed peak of the iron(III) to iron(II) reduction was observed. The anti-peak of the produced Fe(II) back reoxidation appeared at the potential of about -0.3 V vs. SCE and its magnitude is substantially lower as that of cathodic peak. From this fact as well as from the anodic/cathodic peak potentials difference together with a peak
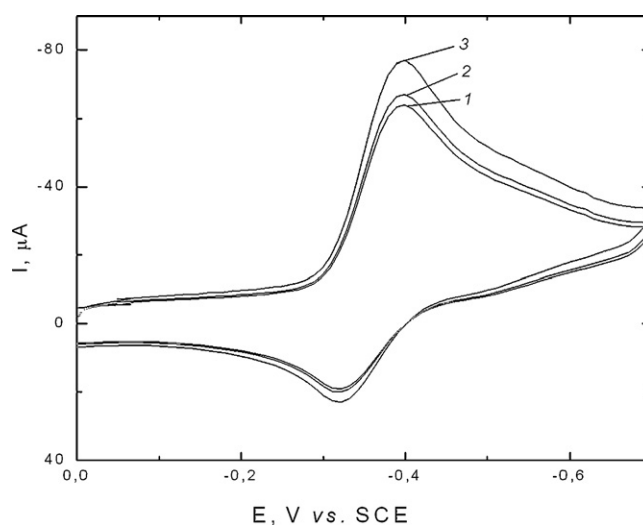

Fig. 3. Cyclic voltammograms of 2×10^{-3} mol dm^{-3} Fe^{3+} in 0.2 mol dm^{-3} NaCl; curve 1 – one segment of IDA, curve 2 – second segment of IDA, curve 3 – interconnected both IDA segments.

potential shift dependence on scan rate it can be concluded that the kinetics of charge transfer through electrode–solution interface is slower than in the case of reversible redox species and Fe(III)/Fe(II) redox couple behaves on platinum IDA as a quasi-reversible system.

Then the diffusion layer overlapping due to non-linear diffusion in IDA array was investigated. Cyclic voltammograms of above-mentioned solution were measured on first and second segment separately (curves 1 and 2 in Fig. 3). As for current magnitude the voltammetric response is practically the same which shows that both segments of IDA are practically identical. When the segments are interconnected (curve 3 in Fig. 3) the response is only a little bit higher than the response for any separate IDA segment. The current magnitude is dramatically lower than the sum of currents measured on both segments separately. This means that a cylindrical character of diffusion transport to the segments of IDA allows an effective exhaustion of electroactive species from the solution above the insulating gaps and the non-interconnected segment. At this condition interdigitated microelectrode array behaves as an electrode with area equal to the sum of both segments areas and the area of insulators between them. This may enhance the sensitivity of measurement because the faradaic signal is proportional to the mentioned sum whereas charging current is proportional to the area of one segment of IDA array. Enhanced faradaic signal to charging noise ratio could thus lower detection limit.

The analytical technique for the detection of fluoride presented in this contribution is based on the chemical complexation of Fe in the solution in which aqueous Fe^{3+} ion reacts with fluoride anion forming fluoroferric complex. This complex is electroinactive at the potential of the reduction of aqueous Fe^{3+} cation. Diffusion current of the reduction of Fe^{3+} to Fe^{2+} is decreased due to its electro-deactivation by complexation with fluoride. This decreasing is proportional to the concentration of free fluoride anion and can be utilized for its detection.

There may occur some interferences in voltammetric as well as in potentiometric analysis of fluoride. Interferences are mainly caused by cations (e.g., Al^{3+}, Si(IV), Cu^{2+}, Fe^{3+}) at very low concentrations forming complexes with fluoride. When such complexation takes place the fluoride content detected is lower. This causes an error of analysis. In potentiometric analysis these interferences are treated by addition of CDTA [17] which forms stronger complexes with the above mentioned cations than fluoride. In our case CDTA additions does not solve the interference problem. In Section 2, we suggested a simple procedure using DOWEX X-4 in H^+ cycle to remove possible interfering cations.

Linear sweep voltammograms of the Fe(III) reduction in the presence of fluoride ions were registered and they are depicted on Fig. 4. At the above-mentioned conditions LSV exhibits a very good repeatability. From 20 consecutive runs average relative standard deviation of peak height of 4% was obtained. The peak height was diminished with increasing concentration of fluoride. This diminishing can be utilized for its determination. The dependence of peak decrease on fluoride concentration was investigated and found to be linear in fluoride concentration in the range from 5×10^{-5} to 8×10^{-4} mol dm^{-3} fitting the equation ABS$(I_n - I_0) = A + B.c_{F^-}$, where the I_0 is the peak current without addition of fluoride, I_n is decreased peak current after n additions of fluoride. Intercept A is equal to 4.2 μA with SD$_A$ = 0.13 μA and the magnitude of slope B is 7988 μA mol^{-1} dm^3 with SD$_B$ = 281.3 μA mol^{-1} dm^3 (R = 0.997). The detection limit calculated according to 3 SD$_A$ criterion was estimated to 4.5×10^{-5} mol dm^{-3}.

We also tried to establish a rough concept of amperometric variant of this technique in the stirred solution. We studied the amperometric response of interdigitated microelectrode array at three potentials −0.4, −0.5 and −0.6 V vs. SCE. The last one seems to be optimal because at this potential a slightly higher repeatability was observed as compared to the less negative potential
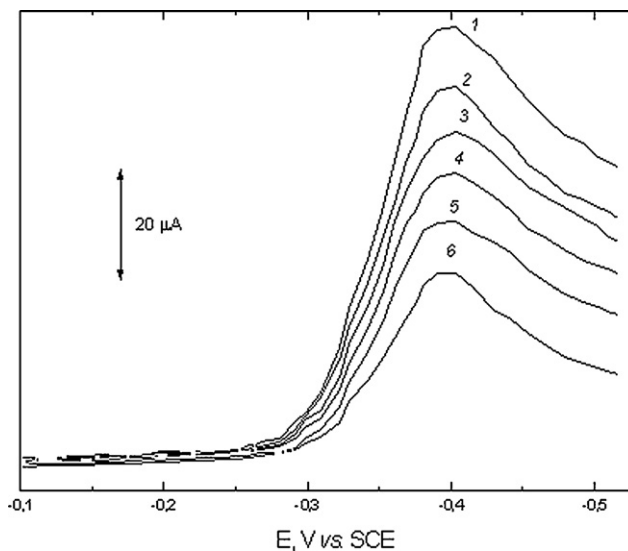

Fig. 4. Fluoride influence on IDA voltammetric response of the Fe^{3+} reduction. Voltammograms of 20 mL of 2×10^{-3} mol dm^{-3} Fe^{3+} in 0.2 mol dm^{-3} NaCl in voltammetric cell with additions of 0.25 mol dm^{-3} NaF solution 1 – no fluoride, 2 – 0.1 mL, 3 – 0.2 mL, 4 – 0.3 mL, 5 – 0.4 mL, 6 – 0.5 mL.

values. Therefore at further experiments this value (−0.6 V vs. SCE) was used to register current–time dependences. Amperometric response of iron(III) was also found to be sensitive to fluoride additions (Fig. 5), however, the current fluctuations appeared when the solution was stirred. Observed sensitivity IDA to fluctuations of convection could be significant limitation to this determination. Detection limit of 2.4×10^{-4} mol dm^{-3} was estimated from the dependence of current on fluoride concentration using the same criterion as in voltammetric mode. It is still one order lower than in the case classical polarometric titration on platinum macroelectrode [18]. This is caused by cylindrical diffusion, exhaustion of electroactive species from the solution above the insulating gaps
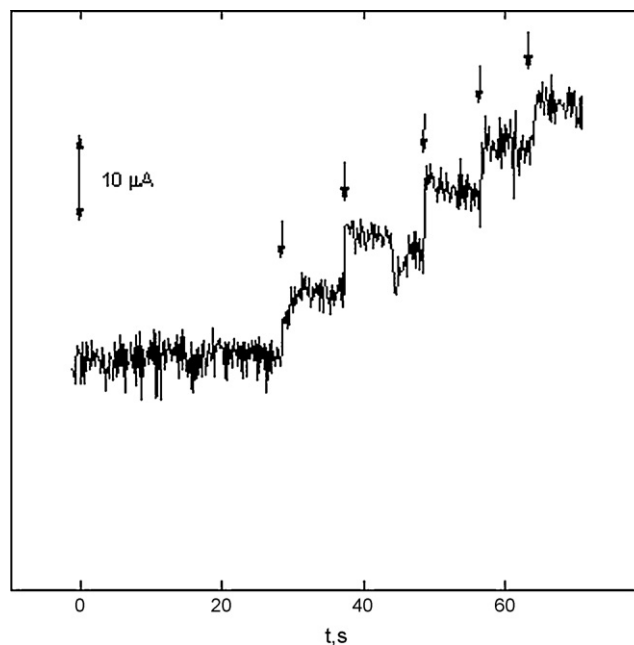

Fig. 5. Fluoride influence on IDA amperometric response of the Fe^{3+} reduction. The limiting current time dependence of stirred solution 20 mL of 2×10^{-3} mol dm^{-3} Fe^{3+} in 0.2 mol dm^{-3} NaCl in voltammetric cell with stepwise additions mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL of 0.25 mol dm^{-3} NaF solution marked with arrows.

Table 1
Model samples analysis (6 parallel determinations of each model sample).

F$^-$ content [mg]	F$^-$ content (found) [mg]	SD [mg]	Confidence interval for 95% probability, [%]
0.5	0.48	0.09	96 ± 19
1.0	1.05	0.14	105 ± 17
1.5	1.45	0.17	97 ± 12
2.0	2.08	0.24	104 ± 14

Table 2
Real samples analysis of fluoride content in toothpaste.

Sample	F$^-$ content[a] [μ/g]	SD [μ/g]	F$^-$ content[b] [μ/g]	SD [μ/g]	F$^-$ content[c] [μ/g]
A	1352	151	1388	127	1450
B	1349	126	1361	118	1400
C	441	39	459	29	500

A: Signal Crystal Gel Fresh & White, Unilever Slovakia, Bratislava, Cintorínska 3/B; B: Sensodyne F – Fluoride, GlaxoSmithKline, Czech Republic, Prague; C: Aquafresh Kids, GlaxoSmithKline, Czech Republic, Prague.

[a] Determined by this method.
[b] Determined by ISE potentiometry as an independent method.
[c] Declared by manufacturer Number of analyses is 4 for both voltammetric and potentiometric methods.

and non-interconnected segment. Poor repeatability was obtained from 20 consecutive runs an average relative standard deviation of 20% has been reached. Reproducibility of amperometric variant was also tested on a real sample (one sample, 4 analyses), however the relative standard deviation more than 20% hardly enables to compete with the voltammetric method. That is why LSV was preferred for fluoride analysis in toothpaste.

Model samples analysis was performed for validation of the developed voltammetric technique. The results are summarized in Table 1. Four samples of 20 mL of NaF solutions with fluoride content of 0.5 mg, 1.0 mg, 1.5 mg and 2.0 mg were analyzed. Multiple standard addition method was used for obtaining the concentration in all analysis. The mean of six parallel determinations does not statistically differ from taken values.

Toothpastes from three different producers served as real samples. Multiple standard additions were used for F$^-$ content evaluation. To avoid possible effect of matrix standard F$^-$ additions were added directly to the weighed toothpaste sample into a 100 mL teflon beaker in process of sample solution preparation as described in Section 2. The results of their analysis are in Table 2. Analyses were performed voltammetrically in an unstirred solution (LSV). Good reproducibility of real samples analysis is shown in Table 2, relative standard deviation of 8–11% was achieved. All samples were also analysed potentiometrically with fluoride selective ISE. The results obtained by presented voltammetric technique are in good agreement with results obtained by ISE potentiometry. Fluoride content determined by both techniques does not substantially differ from that declared by the manufacturer. Our method based on dynamic electrochemistry can be considered a faster and more precise alternative to ISE potentiometry in the fluoride content monitoring.

4. Conclusions

Platinum comb-shaped interdigitated microelectrode array (IDA) was used in development of the method for the determination of fluoride. Proposed technique is based on decreasing of reduction current of aqueous iron(III) in NaCl solution after its complexation with fluoride forming electroinactive fluoroferric complex. Detection limit of 4.5×10^{-5} mol dm^{-3} was obtained in the voltammetric variant of the technique in quiet (unstirred) solution. Amperometric variant has detection limit of 2.4×10^{-4} mol dm^{-3} because large current fluctuations appeared when the solution is stirred. The method was applied to the analysis of toothpaste. This method based on dynamic electrochemistry can be considered a faster and more precise alternative to ISE potentiometry.

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