Analytical, Nutritional and Clinical Methods Section

Polarographic determination of trace fluoride in foods

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Abstract

This paper describes a polarographic method for the determination of trace of F^- in mineral water, tap water, table salts, maize and rice using a dropping mercury electrode(DME). In $La(III)-ALC-(CH_2)_6N_4$ system (pH = 4.9), $(LaALC)_2F_2$ complex gave a peak potential at -0.64 V versus SCE. The peak height was directly proportional to F^- in the concentration range 8×10^{-8} M–1×10^{-6}M. The limit of detection was 5×10^{-8} M. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The role of fluorine as an important trace element in the human body has been investigated. Many methods for the determination of fluoride have been reported. A fluoride-selective electrode was used for the determination of trace fluoride. However, the sensitivity of these methods is not very high and the range of detection is only about 5×10^{-6}–2×10^{-5} M (Alberto, 1988; Arabadzhi, Enanan, Dzerzhko & Voloshchuk, 1989; Bilal & Langer, 1988; Carvalho, Polizello, Caldeira & Spadaro, 1997; Conde, 1989; Gulubova, 1990; Guo & Nie, 1988; Hino, Nakanishi, Nagashima, 1992; Lopez & Navia, 1988; Ramados, Balaji, Gomathy & Ramaninh, 1989). Another analytical method that can be used to determine fluoride is spectrophotometry (Babas Pardillo, Peris Martinez, Gimeno Adelantado & Bosch Reig, 1989; Culik, 1986; Ferris, Bingham & Leonard, 1988; Gomez Gomez, Palacios Corvillo & Camara Rica, 1991; Hong and Wang, 1987; Rastogi, Mhatre, Mahajan, Chanudhuri & Pati, 1991; Salem, 1996), but the sensitivity is poor. Recently, a polarographic method for the determination of fluoride has been reported (Li & Shang, 1986). However, reaction equilibration was required for about 2 h before the potential scan was carried out. The linear range of the method is 1×10^{-7}–6×10^{-6}M. In addition, stripping voltammetry can be used for fluoride determination (Wang & Grabaric, 1990), but this method is often time-consuming (preconcentration time) in the analytic procedure. In this

report, we have investigated the electrochemical behavior of $(LaALC)_2F_2$ complex by different electrochemical methods. The reaction is equilibrated for about 20 min before the potential scan is carried out. The peak height is directly proportional to the fluoride concentration over the range 8×10^{-8}–1×10^{-6} M, with a detection limit of 5×10^{-8} M.

2. Materials and methods

2.1. Apparatus

A Model JP-2A oscillopolarograph (Chengdu Instrumental Factory,China)and a three-electrode system with a dropping mercury working electrode (DME) were used. The reference and counter electrodes were saturated calomel and platinum wire electrodes. A Model 82-1 voltammetry and a pHs-3 meter were used. The electrolytic cell was a 10 ml beaker.

2.2. Reagents

All the reagents used are of analytical reagent grade. Triply distilled water is used for the preparation of all solutions.

Standard fluoride solution(1×10^{-2} M); dissolving 0.1042 g of sodium fluoride in 250 ml of water.

La (III) solution(5×10^{-3} M); dissolving 0.0815 g of La_2O_3 in 100 ml 2 M HNO_3, diluting to 5×10^{-4} M with water before use.

Alizarin complexone (ALC) solution(1×10^{-3} M); dissolving 0.0386 g of ALC with 2 M sodium hydroxide

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and neutralizing the solution to a yellow color with 2 M nitric acid, and then diluting to 100 ml with water. Diluting to 1×10^{-4} M with water before use.

Hexamethylene tetramine $[(CH_2)_6N_4]$ solution (1.1 M); dissolving 70 g of $(CH_2)_6N_4$ and 50 g of potassium nitrate in 450 ml of hot water,and then adjusting the pH to 4.9 with 2 M nitric acid.

Acetone—analytical reagent grade.

2.3. Analytical procedure

Pipette the standard or sample solution of fluoride into a 10 ml beaker, add 1 ml of 1.1 M $(CH_2)_6N_4$,1.5 ml of 1×10^{-4}M ALC,1.2 ml of 5×10^{-4} M La(III) and 1 ml of acetone. Allow to stand for about 20 min and then dilute the solution to 10 ml with water. The derivative single sweep polarogram is recorded from -0.30 V to -0.80 V (vs SCE) and the peak height is measured at -0.64 V (Fig. 1).

2.4. Analysis of samples

Mineral water and tap water were directly used for the fluoride determination. For the determination of fluoride in table salts, 5 g of the salts were dissolved in 100 ml water. The solutions were taken as the test solutions. For the fluoride determination in maize and rice, the samples were prepared according to the national standards of P.R.China(Methods of food hygienic analysis—physical and chemical section) (Hygienic bureau of P.R. China, 1997) prior to the polarographic determination. Six grammes of ground maize or rice was weighed into a 30 ml porcelain crucible, 5 ml 10% $Mg(NO_3)_2$ (fixed fluoride agent) and 0.5 ml of 10% NaOH were added. The solution is alkali. The solution was evaporated to dryness on a water-bath, carbonized at low temperature and the crucible was transferred into a muffle furnace for heating at 600°C for 6 h. After cooling 10 ml water was added to the crucible, and

neutralized with H_2SO_4 (2:1) until no bubbles were generated. The solution was transferred to a 250 ml distillation flask, 60 ml H_2SO_4 (2:1) was added with some glass beads. The distillate was absorbed by 5 ml 2% NaOH in a 50 ml beaker. The distillation was completed when the temperature of the flask contents reached 190°C (whole distillation time:15–20min). The condenser was removed, and the solution was transferred into to a 100 ml volumetric flask, neutralized to neutrality with HCl (1:11), and then diluted to 100 ml with water. The solution was analysed for fluoride. All the results are summarized in Table 1.

A fluoride ion-selective method (Wan , Lu, Zen, & Song, 1992) is used for comparing the results. A total ionic strength adjustment buffer(TISAB, pH = 5.3, 20 ml) was added to 50 ml of the sample solution(maize and rice, 20 ml) and stirred continuously, while the electrochemical potential was measured with an ion-selective fluoride electrode. Using the standard addition technique the concentration of fluoride in the samples was calculated (see Table 1).

In order to evaluate the validity of the proposed method to determine fluoride in foods, recovery studies were carried out on samples to which known amounts of fluoride had been added. The results are summarized in Table 1. In most cases recovery was higher than 90%, with a mean recovery of 96.9%, which indicates, the validity of the proposed method.

3. Results and discussion

3.1. Selection of experimental conditions

The effects of pH and the concentration of La(III) and ALC on peak height are shown in Figs. 2,3 and 4, respectively. The optimum conditions for the determination are 6×10^{-5} M La(III) and 1.5×10^{-5}M ALC.
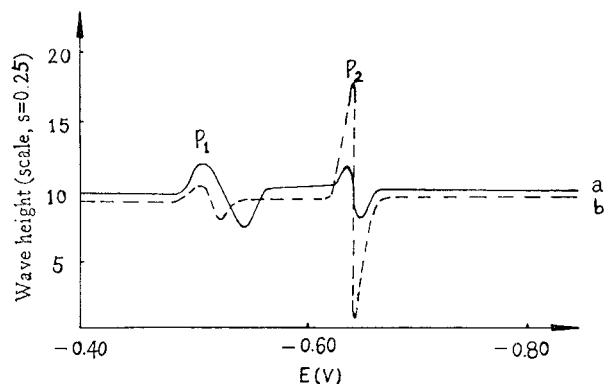

Fig. 1. Polarographic waves; a.pH = 4.90 6.0×10^{-5} M La^{3+} + 1.5 $\times 10^{-5}$ M ALC; b.pH = 4.90 6.0×10^{-5} M La^{3+} + 1.5×10^{-5} M ALC + 1.0×10^{-6} M F$^-$; p$_1$,La(III)−ALC binary complex peak; p$_2$, La(III)−ALC−F$^-$ternary complex peak, S:Current sensitive.

Table 1
Determination of F$^-$ in Samples ($n = 6$)

Sample	Present method (μg/g or μg/ml)[a]	Recovery (%)	Fluoride selective electrode (μg/g or μg/ml)
Mineral water (Wahaha)	0.14 ± 0.03[b]	90.0	0.15
Tap water	0.18 ± 0.06	96.0	0.19
Table salt (Hubei)	0.125 ± 0.012	90.1	0.138
Table salt (Yincheng)	0.443 ± 0.017	94.4	0.476
Maize	5.91 ± 0.36	104.0	6.18
Rice	4.62 ± 0.28	106.7	4.43

[a] μg/g for salts, maize and rice and μg/ml for tap water and mineral water.

[b] : ± Standard deviation.
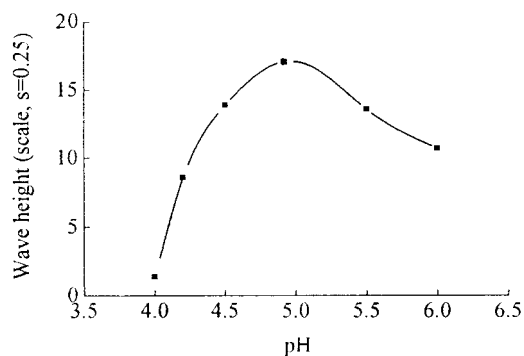
Fig. 2. Effect of acidity on peak current; 6×10^{-5} M La(III) + 1×10^{-6} M F$^-$ + 1.5×10^{-5}M ALC. S: Current sensitive.

Fig. 3. Effect of La(III) concentration of peak current; 1.5×10^{-5}M ALC + 1.0×10^{-6}M F$^-$ (pH = 4.9). S: Current sensitive.
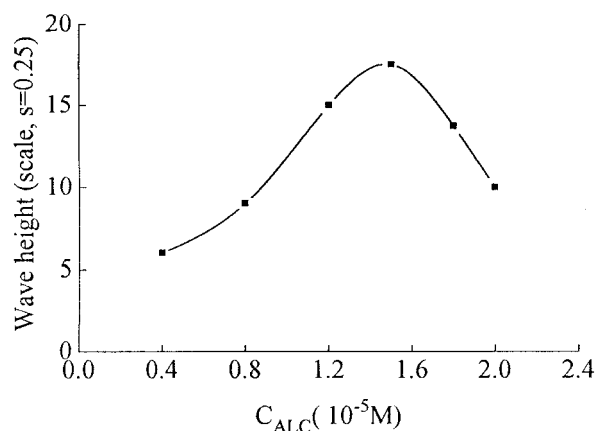

Fig. 4. Effect of ALC concentration on peak current; 6×10^{-5} M La(III) + 1.0×10^{-6}M F$^-$ (pH = 4.9). S: Current sensitive.
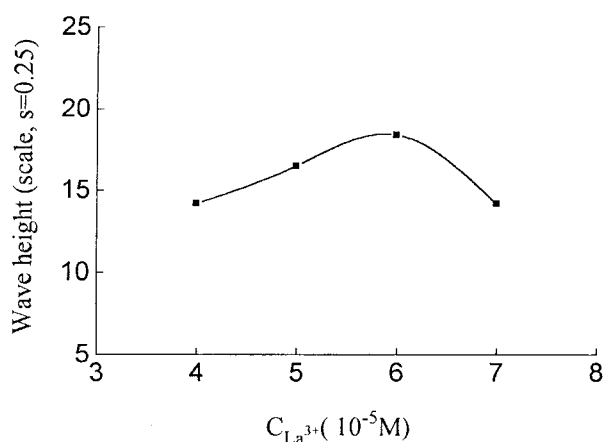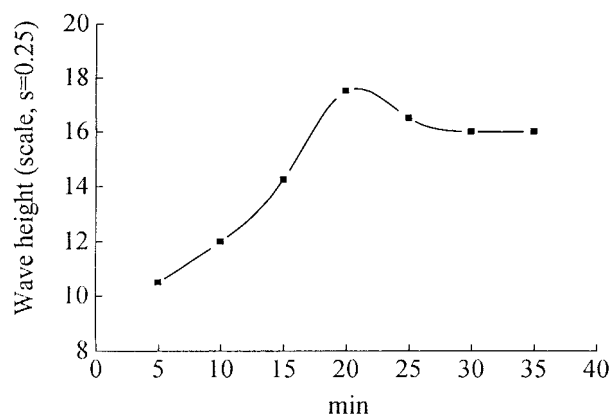

Fig. 5. Choice of stable time; 1.5×10^{-5} M ALC + 6.0×10^{-5} M La(III) + 1.0×10^{-6} M F$^-$ (pH = 4.9). S: Current sensitive.

Fig. 2 shows that the polarographic peak almost disappears when the pH is 4, so the optimum pH is about 4.9. It was also found that acetone can increase the peak height and shorten the formation time of the La(III)-ALC-F$^-$ ternary complex. The optimum concentration of acetone is 10%.

3.2. Effect of standing time

In order to obtain a stable polarographic peak, the solution to be analysed was required to stand for some time; a 20 min period was found to be optimum (Fig. 5).

Under the selected conditions, the relationship between peak height and concentration of F$^-$ was linear from 8×10^{-8} to 1×10^{-6} M. The regression equation of the calibration line has the form:

$$y = 1.76 \times 10^7 x + 0.0586$$

Where y is the peak height (scale, $s = 0.25$) and x is the concentration of fluoride (M). The correlation coefficient was 0.999. A detection limit of 5×10^{-8} M was obtained.

3.3. Interferences

The experimental results show that 1250-fold NO$_2^-$; 1000-fold K$^+$, Na$^+$, Ag$^+$, Ca(II), Sr(II), Cl$^-$ and NO$_3^-$; 500-fold Mg(II) and Br$^-$; 100-fold I$^-$ and SO$_4^{2-}$; 75-fold Co(II); 50-fold Cr(III) and Mo(VI) and 40-fold As(V) have no effect on the determination of F$^-$ (1×10^{-6} M). In contrast,100-fold Pb^{2+}; 50-fold Fe^{3+} and 25-fold Al^{3+} have great interference with the determination, causing an obvious decrease of the peak current.

3.4. Formation of a polarographic wave

In the presence of ALC and La(III),La(III)reacts with ALC to form a purplish red binary complex, the complex has stronger adsorption at a mercury electrode and produces the reductive peak p_1(−0.54 V) and oxidative peak (−0.52 V) (Fig. 6).When a trace F$^-$ is added to the solution containing La(III) and ALC, another reductive peak p_2 appears at −0.64 v. This suggests that peak p_2 is caused by the La(III)-ALC-F$^-$ purplish blue ternary complex. The peak height of p_2 increases with increasing
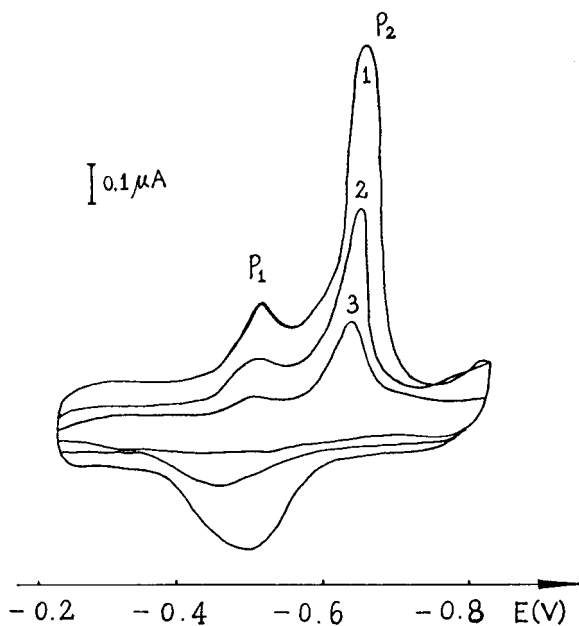
Fig. 6. Cyclic voltammograms. Experimental conditions as for Fig. 1, except for F$^-$,1.0×10^{-5} M Scan rate, 50 mV/s. p$_1$, La(III)−ALC binary complex; p$_2$, La(III)−ALC-F$^-$ ternary complex.

Fig. 7. Electrocapillary curves. Curve 1: ALC solution (1.5×10^{-5} M), 0.1 M(CH$_2$)$_6$N$_4$,10% acetone, pH = 4.9; Curve 2: 1 + La(III)(6.0×10^{-5} M); Curve 3: 2 + F$^-$ (6.0×10^{-7} M).

F$^-$ concentration, so peak p_2 can be applied to the determination of trace F$^-$. The composition of the ternary complex has been obtained to be (La ALC)$_2$F$_2$ by spectrophometry (Langmyhr, Klausen, & Nouri-Nekoui, 1971):
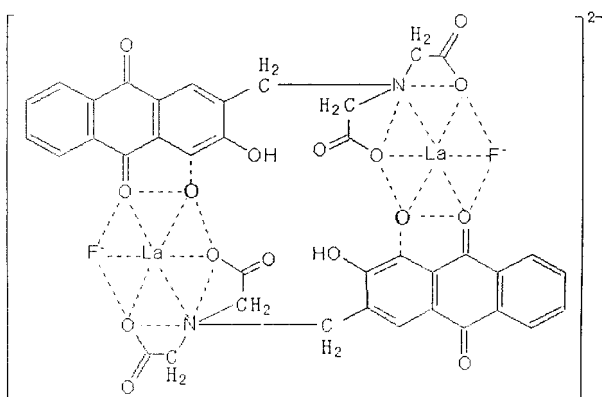

In the molecule of (La ALC)$_2$ F$_2$ there are four quinone groups, with reference to the work of Li and Shang (1986), the reaction scheme may be as follows:

(La ALC)$_2$*F$_2$⇌(La ALC)$_2$F$_2$ads.
(La ALC)$_2$F$_2$ads. + 4e + 4H$^+$ = (La ALC′)$_2$F$_2$
* ALC: quinone anion ALC′: hydroquinone anion

3.5. Properties of a polarographic wave

Electrocapillary curves can give some characteristic information about the adsorption of a particular species. A solution containing F$^-$ has an electrocapillary curve lower than that of the supporting electrolyte (Fig. 7; Curves 1,2,3) because the adsorption of the (La ALC)$_2$F$_2$ complex on the surface of the DME changes the surface tension of the mercury drop.This clearly illustrates the adsorption of (La ALC)$_2$F$_2$ at the DME.

The cyclic voltammetry of the system was investigated with a Model 82-1 voltammetric analyser with a hanging mercury drop electrode. The complex gives a cathodic peak at about −0.64 V (vs SCE). No peak was observed on the anodic branch, indicating irreversibility of the reduction. The cathodic peak in the first scan was much higher than that in the following scans (Fig. 6; Curves 1,2,3). Furthermore, the experimental results show that the same polarographic waves can be obtained with a glassy carbon electrode or a carbon paste electrode as a working electrode. All these phenomena give evidence of the adsorption character of the polarographic wave.
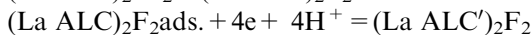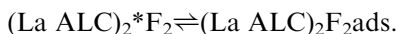
4. Conclusion

Experimental results have demonstrated that the proposed polarographic method is simple and accurate for the determination of fluoride in foods. The results obtained by this method are in good agreement with those obtained by the ion-selective electrode method. Compared with the ion-selective electrode method, this method is more sensitive and the sample solution needed for fluoride determination is much less.

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