EFFECT OF SOME MASKING REAGENTS IN THE QUANTITATIVE DETERMINATION OF FLUORIDE IN WATER BY ION-SELECTIVE ELECTRODE

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SUMMARY. A rapid and selective method has been used for the determination of fluoride by ion-selective electrode. The appropriate pH range for the analysis was 4.5-6.0. The complexing agent studied, tri-sodium citrate, was observed to be the most efficient masking agent for Al, Fe, Ca and Mg. Even a large excess of elements with high stability constant does not interfere with it. The accuracy and precision of the method was evaluated. The method has been applied for drinking and river water samples.

Key-words: Fluoride, ion-selective electrode, buffer solutions, water

INTRODUCTION

Fluorine is extensively distributed throughout nature, and has been detected in several matrices, such as water, rocks, foodstuffs and biological samples[1, 2, 3].

The determination of fluoride in water is of considerable interest and the advent of ion-selective electrode simplified the analysis considerably, because it can be analyzed by direct potentiometry with excellent selectivity.

The determination of traces of fluoride in solution with ion selective electrode involves certain difficulties due to the slow electrode response[4,5] and due to the necessity of separating fluoride from interfering ions by the formation of strong metal-fluoride complexes with cations such as Al, Fe, Ca and Mg including the hydrogen ion. In addition, the electrode is also sensitive to the hydroxide ion generally present in environmental samples.

In practice, these effects can be minimized by adding a buffer solution (TISAB - Total Ionic-Strength Adjustment Buffer) to maintain the pH at around 5 and HF, H_2F_2 and HF_2 - formation, which occurs at and below pH 5, reducing the fluoride ion activity in the solution[6].

The purpose of this work was to study the influence of masking reagents, citrate, sulfosalicylate, triethanolamine, CDTA, EDTA, phosphate, aluminon to determine fluoride with sufficient reproducibility and sensitivity in presence of Al, Fe, Mg and Ca in drinking and river water samples. The method is simple, rapid, reliable and accurate.

MATERIALS AND METHODS

Apparatus

Orion fluoride selective electrode model 94-09-00 and reference electrode Orion model 90-00-01 Ag/AgCl , with internal solution of KCl connected to an ion analyzer Procyon, model E-920.

Stock fluoride solutions and Stock interfering ion solutions

Aqueous solutions of NaF 1M, NaF previously dried at 120°C for 8 h. Standard solutions were prepared by sequential dilution of the stock solution. Solutions of interfering ions Al, Fe, Ca, and Mg were prepared as 1 mg/L aqueous solutions of the respective ion. The solutions were prepared from nitrate or sulfate.

Buffer solutions

All buffer solutions were adjusted to pH 5.5 with NaOH or HCl, except TISAB-7 and SSA/EDTA, with NH_4OH, and diluted to 1L with water.

TISAB-1[7]: Dissolve 58 g NaCl and add 57 mL glacial acetic acid.

TISAB-2: tri-sodium citrate[8,9] : Dissolve 58 g NaCl, add 57 mL glacial acetic acid, and: 2.941 g (0.01 M), 29.41 g (0.1 M), 117.6 g (0.4 M) and 294.1 g (1 M) tri-sodium citrate.

TISAB-3, tris[8,10]: Dissolve 242 g tris(hydroxymethyl) aminomethane and add 230 g sodium tartrate.

TISAB-4, aluminon[8]: Dissolve 58 g NaCl add 57 mL glacial acetic acid, 10 g aluminon, and 29.4 g tri-sodium citrate.

TISAB-5, citric acid[11]: Dissolve 58 g NaCl, add 57 mL glacial acetic acid, and 84.1 g citric acid.

TISAB-6, CDTA[10,11,12]: Dissolve 385 g ammonium acetate add 13.5 mL HCl, and 19.8 g CDTA.

TISAB-7, SSA/EDTA[8,10]: `Dissolve 204 g sulfosalicylic acid and add 74 g EDTA.

TISAB-8, triethanolamine[13] : Dissolve 240 g triethanolamine.

Phosphoric acid[14]: 1M and 5M.

RESULTS AND DISCUSSION

Response time of the electrode

The potential plateau was generally achieved within three minutes after buffer addition for fluoride higher than 10^{-4} M. For solutions with fluoride lower than 10^{-5}M in buffers of triethanolamine 0.5M and citrate 0.4M the plateau was achieved in 30 min. and 15 min., respectively.

Effect of pH

In order to study the influence of pH closely; a series of TISAB buffer solutions with different acidities were prepared. The electrode potentials were observed in these solutions with varying concentration of fluoride from 10^{-7} to 10^{-3} M. The results presented in Figure 1 show that in basic solutions and lower than 10^{-5}M concentration of fluoride, the electrode responds mainly to changes in the hydroxide ion concentration. An optimum pH appears to be around pH 5. In this paper all the experiments were made using pH 5.5.
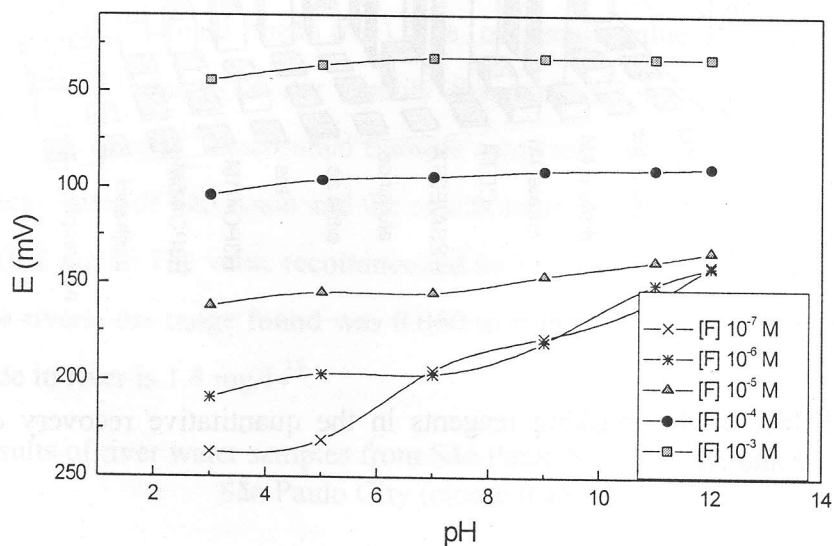

Figure 1 Influence of pH on electrode potential in citrate 0.4M in presence of differents added fluoride amounts.

Effect of interfering ions

According to many investigations Al is the most common and serious interference in fluoride[15].

At higher metal concentrations, Fe, Ca and Mg may also interfere. To study the influences of Al, Fe, Ca and Mg in the determination of fluoride synthetic samples solutions containing a small amount of fluoride were prepared. The maximum amount of interfering cations to obtain a quantitative recovery of fluoride in different TISAB solutions were studied. The results are presented in Figure 2. By examining the results it can be said that from all the elements studied, Al is the most serious interfering, which forms strong fluoride complexes, TISAB citrate 0.4M and 1M being more effective.
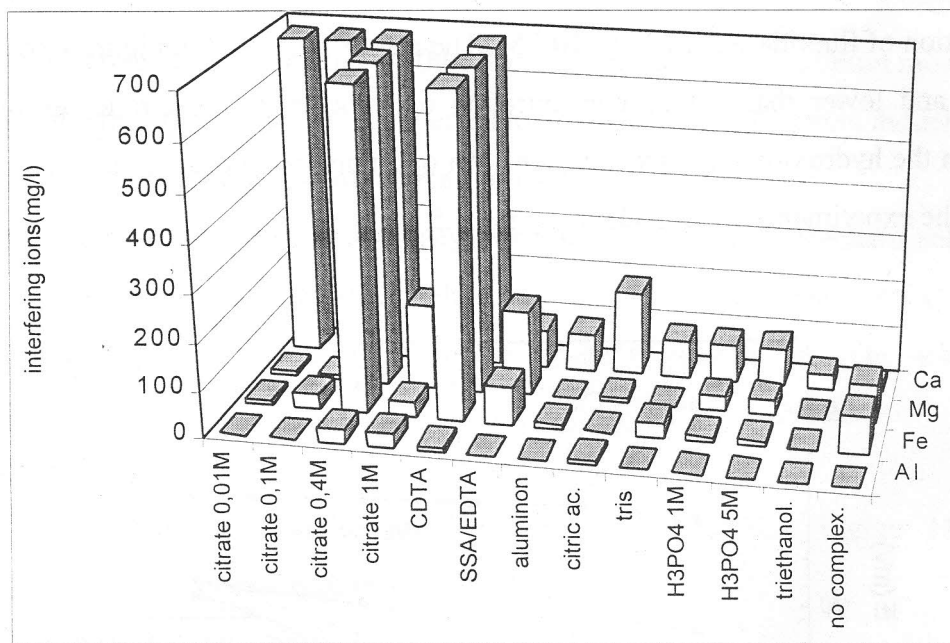

Figure 2   Effect of the masking reagents in the quantitative recovery of fluoride in presence of Ca, Mg, Fe and Al.

Precision and accuracy

The precision and accuracy of the method was tested by analyzing Rainwater, NIST-SRM-2694aII. The precision was demonstrated by the relative standard deviation evaluated through 7 determinations. The accuracy was verified by the relative error. As shown in Table 1, both RSD and relative error are less than 5% indicating high precision and high accuracy of the method.

Table 1 Results for simulated rainwater NIST – SRM – 2694aII

TISAB	Certified value [F⁻] µg/L	Found [F⁻] µg/L	RSD (%)	Relative error (%)
Citrate 0,4M	0,108±0,004	0,100 0,100 0,099 0,100 0,110 0,110 0,100 0,103±0,005	4,9	4,6

RSD – Relative standard deviation

APPLICATIONS

To show the applicability of the method to real samples, it was applied to the determination of fluoride in drinking water used in São Paulo's public supply system and in river water; Table 2 shows the concentrations found (mean n=3). The maximum value recommended for fluoride in the Brazilian Federal Drinking Water Quality Standard is 1.4 mg/L[25] ; the value found was 0.71±0.01 mg/L. Pires et al[17] determined fluoride using ion chromatography in 19 districts from five geographical zones of São Paulo and the results found ranged from 0.09 to 0.58 mg/L with a mean of 0.4 ± 0.2 mg/L. The value recommended by European Community at 25 to 30 °C is 0.7 mg/L. For the rivers, the range found was 0.060 to 0.158 mg/L and the maximum permissible level of fluoride in river is 1.4 mg/L[18].

Table 2 Results of river water samples from São Paulo State and supply drinking water from São Paulo City (citrate 0.4M, n=3).

Sample	[F] µg/mL
Jaguari-mirim River	0.136±0.009
Doce River	0.060±0.002
Itobi River	0.158±0.008
Supply drinking water	0.71±0.01

CONCLUSION

To study the influence of Al, Fe, Ca, and Mg in the determination of fluoride synthetic sample solutions containing a definite small amount of fluoride and large amounts of interfering ions were studied. As it can be seen in Figure 2, the most serious interference is caused by Al due to the formation of AlF_6^{3-} complex with high stability, $log\beta = 19.84$. From the studied TISAB , tri-sodium citrate 0.4M and 1M with pH 5.5 were the most effective for fluoride determination.

Although Fe forms FeF_3 complex also with high stability, $log\beta = 12.06$, it is possible to determine fluoride with citrate 0.4M and CDTA. As expected, Ca caused less interference, because it forms CaF_2, $log\beta = 1.04$, being complexed with citrate, CDTA, aluminon and citric acid. Magnesium had a behavior similar to that of Fe, and could be masked with more concentrated solutions of citrate, CDTA and SSA/EDTA. The buffers, tris, phosphoric acid, and triethanolamine presented little efficiency in complexing the studied cations.

By comparing all the studied masking reagents it could be concluded that citrate 0.4M and CDTA presented high sensitivity in fluoride determination; however, citrate 0.4M was more effective for Al. The reproducibility was better than 5% similar to that obtained by other methods. This work confirms that citrate is an ideal agent for this purpose, it is efficient, inexpensive, available at high purity, and can be, if necessary, prepared as a fairly concentrated solution.

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