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Analytical Methods Section

Direct potentiometric determination of fluoride in beverages. Comparative study of different buffering solutions

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A comparative study of different buffering solutions was carried out for the direct potentiometric determination of the fluoride content of beverages manufactured on the island of Tenerife: beer and soft drinks. The technique used was that of standard additions. The accuracy and precision for each of the solutions tested is expressed in terms of average and standard deviation of recovery percentages. Orthophosphoric acid (0·75 M) stood out as the optimum buffering solution. Potentiometry, preceded by heat-facilitated diffusion with or without incineration of the sample, was used as a reference technique. With the exception of beers, all fluoride in the rest of the beverages was present in unbound ionic form; it is therefore detectable through direct potentiometry.

INTRODUCTION

Normally both beers and soft drinks contain low levels of fluoride (Postel *et al.*, 1976; Schulz *et al.*, 1976) which depend essentially on the levels of this substance in the waters used for their manufacture (Postel *et al.*, 1976; Schulz *et al.*, 1976; Clovis & Hargreaves, 1988). However, a precise assessment of the total fluoride intake needs to take into account all the sources: foods, beverages, air, etc.

The appearance of the fluoride selective electrode has considerably simplified these determinations. Under certain conditions of total ionic strength, pH, etc., it allows the direct detection of fluoride in the original sample, thus eliminating the tedious distillation that used to be necessary for the application of classical techniques. This necessitates the use of buffer solutions which have a triple function: to provide and maintain a suitable pH, to increase the total ionic strength of the media, and to eliminate certain cations, such as Al^{3+}, Si^{4+} and Fe^{3+}, which bind with the fluoride anion and cause interference. But even under these conditions one of the main problems encountered is the fact that the selective ion electrode is only sensitive to unbound ionic fluoride, and is therefore unable to detect any fluoride which may exist in a combined form in complex matrices.

This work describes the behaviour of the selective ion electrode with different buffer solutions in terms of accuracy, precision and response time for the direct potentiometric determination of the fluoride content of beverages: beer, carbonated beverages and natural apple juice. The technique of standard additions has been used, as it offers better results than the extrapolation on a calibrated line when the concentrations to be determined are low. Finally, once the appropriate buffer solution for each beverage has been chosen, the results obtained by the proposed method are compared with those obtained by potentiometry preceded by heat-facilitated diffusion, with and without incineration, for the purpose of determining the content of diffusible acid fluoride (without incineration) and the total fluoride content (with incineration) (Taves, 1983; Singer & Ophaug, 1986).

MATERIAL AND METHODS

Equipment

An Ingold 157205 fluoride selective electrode and Ingold Nr-103-033-020 double junction reference electrode with a Crison 501 pH/mV digital meter were used. The solutions to be measured were thermostated to 22°C and stirred with a magnetic stirrer.

Reagents

Analytical-grade reagents (Merck) were used. Stock fluoride solution, 0·10 M in deionized water. The

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working solutions were prepared via successive dissolutions of the stock.

Orthophosphoric acid 0·75 M in deionized water.

TISAB (total ionic strength adjustment buffer) solution. The following are the chemical compositions of these solutions: TISAB-Citrate buffer 0·25 M. A total of 73·5 g trisodium citrate 2-hydrate, 37·3 potassium chloride, 10 ml of glacial acetic acid and 10 ml of 20% NaOH solution in 1 litre of deionized water. The pH of this solution should be between 5·0 and 6·0.

TISAB-Tris (Tris buffer). A total of 242 g tris-hydroxyl methyl aminomethane (Tris), 230 g disodium tartrate 2-hydrate and 84 ml HCl (36%) were dissolved in 1 litre of deionized water. This solution had a pH of 8·0.

Analytical procedures

The analytical technique used is based on the determination of potential before and after the addition of a known amount of fluoride to the mixture of a sample and a specific buffering solution. Table 1 shows the buffering solutions used for each different type of beverage and the ratio sample volume (in ml)/volume of buffering solution (in ml).

The additions of fluoride were made from fluoride solutions of 0·01 and 0·001 M.

The following mathematical formula was used to calculate the concentration of fluoride present in the samples:

$$C_{F^-}\,(\mathrm{mg/l}) = \frac{V_a C}{V_0(10^{\Delta E/S} - 1)}$$

V_a, C = the volume (in ml) of the added solution and its concentration (mg litre^{-1})
V_0 = initial volume of the sample (ml)
ΔE = potential increment (mV)
S = slope of the electrode (mV).

The electrode slope (S) was calculated for each buffer solution and for each type of beverage before beginning the analytical procedures, and using the same ratio of volume of the fluoride solution/volume of the buffer solution which would later be used with the sample to be tested. The following procedure was used: both the ion selective and reference electrodes were first placed in a mixture of 0·1 mg fluoride solution/buffer solution to be used, taking note of the potential once the reading had become stable. Secondly, the potential was measured after washing and drying the electrodes in deionized water and in a mixture of 1 mg litre^{-1} of fluoride solution/buffer solution in the same proportion as before. If the electrode is working optimally the difference between both potential readings should range between 56 and 59 mV, depending on the temperature at which the readings were taken. In our case and at a temperature of 22°C, the gradient reading was 59 mV.

Table 1. Conditioning solutions used for the tested beverages and ratio (in ml) for sample volume/volume of conditioning solution

Drink	Conditioning solution	Ratio (ml)
Beer	Orthophosphoric acid 0·75 M	5/1
	TISAB-Citrate 0·25 M	1/1
	TISAB-Tris	1/1
Soft drinks	Orthophosphoric acid	5/1
	TISAB-Citrate 0·25 M	1/1

Once the difference in potential and the electrode slope were known, we applied the ratios sample/buffer solution shown in Table 1 and the technique of standard additions to the aforementioned mathematical formula for the purpose of calculating the fluoride concentration of 11 samples of each of the following beverages: beer, cola, orange and lemon-based soft drinks, aromatized carbonated, bitter and natural apple juice. All of these beverages are manufactured and bottled or canned on the island of Tenerife.

Once the first part of the study had been concluded and having chosen the most appropriate buffer solution for each case, we proceeded to check our results using the heat-facilitated diffusion technique, with and without prior incineration of the sample (Singer & Ophaug, 1986; Taves, 1983) for the purpose of determining whether or not the proposed method would detect all the fluoride present in the samples. This study was also carried out on 11 samples of each type of beverage. The procedure used was as follows:

(a) Heat-facilitated diffusion without prior incineration of the sample (determination of ionic fluoride plus labile acid). The sample (10 ml), in a porcelain capsule and pH adjusted to 8, was dried out at 105°C overnight. The residue was dissolved in 20 ml of 40% perchloric acid (Michele Luise, 1985). Overnight and at a temperature of 55°C we proceeded to collect the fluoride diffused on to a paper filter impregnated with 0·2 ml of 2·5 M NaOH placed in the top of the vial. The alkaline residue was dissolved in 25 ml of deionized water.

(b) Heat-facilitated diffusion with prior incineration of the sample (determination of total fluoride). The sample (10 ml), in a porcelain capsule stabilized with 50 mg of MgO (Taves, 1983) and dried out overnight at 105°C, was incinerated in a muffle incinerator at 450 ± 25°C. The ashes were then dissolved in 20 ml of 40% perchloric acid and the aforementioned procedure was followed.

In order to carry out the potentiometric determination of the fluoride content, the final 25 ml was mixed with the buffer solution which provided the best results for each type of beverage. For each treatment we prepared a blank with 10 ml of deionized water which was subjected to the same treatment.

RESULTS

The accuracy and precision of the analytical procedure for each of the buffer solutions tested is set out in

Table 2. Means and standard deviations of the recovery percentages for beers

Conditioning solution	Means (%) n = 11	σ[a] (mg litre^{-1})
TISAB-Citrate 0·25 M	96·1	2·26
Orthophosphoric acid 0·75 M	99·6	2·23
TISAB-Tris	85·0	2·77

[a] Standard deviation.

Table 3. Comparison between the two conditioning solutions tested: means and standard deviations of recovery percentages for the six types of soft drinks tested

Soft drink	TISAB-Citrate 0·25 M		Orthophosphoric acid 0·75 M	
	Means (%) n = 11	σ (mg litre^{-1})	Means (%) n = 11	σ (mg litre^{-1})
Cola	95·0	1·18	105·6	1·21
Orange	95·6	4·41	99·8	1·21
Lemon	99·6	1·90	101·5	1·51
Bitter	103·9	2·70	100·2	0·60
Carbonated	97·6	4·30	100·1	0·32
Natural canned juice	83·6	1·80	100·0	0·23

Table 2 for beers and in Table 3 for soft drinks. The recovery percentage of added inorganic fluoride, not exceeding 50% of the original fluoride found in the sample, was determined after being put through the entire procedure. These recovery percentages were calculated for each drink sample and for each buffer solution. Accuracy and precision are given in terms of the mean and standard deviation of the aforementioned recovery percentages, respectively.

Figures 1, 2 and 3 present the variation of potential as a function of time. This was used to determine the response time for each buffer solution and for each type of beverage.

From the results exhibited, 0·75 M orthophosphoric acid offers the best results with regard to accuracy, precision and response time. We therefore favour this type

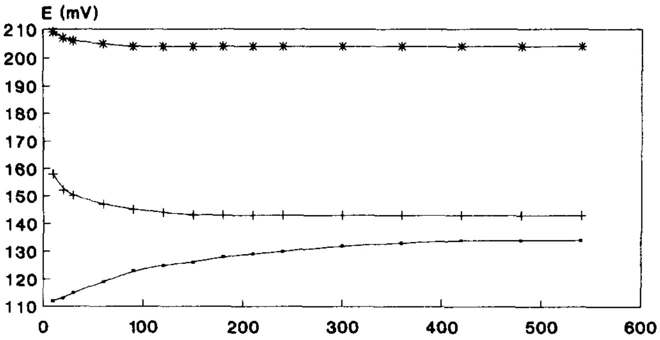

Fig. 1. Potential variation as a function of time in the tests for fluoride in beer. (■, TISAB–Tris; +, TISAB–Citrate; *, Orthophosphoric acid.)

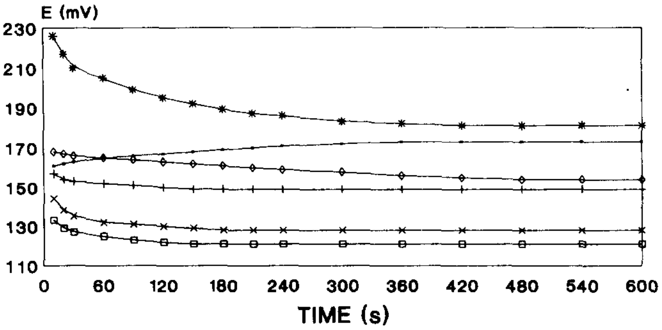

Fig. 2. Potential variation as a function of time in the tests for fluoride in soft drinks using TISAB-Citrate. (■, cola; +, orange; *, lemon; □, bitter; ×, fizzy; ◇, natural canned juices.)

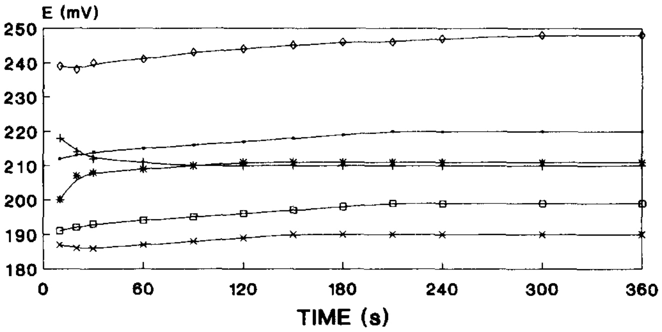

Fig. 3. Potential variation as a function of time in the tests for fluoride in soft drinks using 0·75 M orthophosphoric acid. (■, cola; +, orange; *, lemon; □, bitter; ×, fizzy; ◇, natural canned juices.)

Table 4. Mean fluoride contents obtained through the application of the three analytical procedures used

Procedure	Beer	Cola	Orange	Lemon	Aromatized carbonated	Bitter	Apple juice	R[b] (%)
	Mean[c] fluoride content							
Direct potentiometry	0·45±0·001	0·20±0·000	0·27±0·017	0·30±0·016	0·47±0·021	0·18±0·021	0·11±0·001	97·2
DFC[a] without incineration + potentiometry	0·45±0·030	0·19±0·005	0·27±0·021	0·29±0·033	0·47±0·019	0·17±0·010	0·10±0·025	99·0
DFC[a] with incineration + potentiometry	0·48±0·039	0·20±0·032	0·27±0·025	0·29±0·008	0·47±0·032	0·18±0·007	0·11±0·005	98·6

[a] Heat-facilitated diffusion.

[b] Mean recovery percentage.

[c] Mean concentration ± standard deviation (mg litre^{-1}).

of buffer solution for the potentiometric determination of fluoride in beers and soft drinks.

Table 4 shows the results obtained from the treatment applied to the 11 different samples of each beverage. Direct potentiometry and potentiometry preceded by heat-facilitated diffusion with and without prior incineration of the sample are compared.

We can see that beers show around 6% of bound fluoride which is not detectable by the selective ion electrode. Other beverages show no differences between the levels of free ionic fluoride and total fluoride. Therefore all fluoride present may be determined by the direct potentiometric method. The recovery percentages (Table 4) obtained from the addition of a known amount of inorganic fluoride which does not surpass 50% of the original value of the test sample are valid for the three treatments investigated.

CONCLUSIONS

Direct potentiometry by use of the selective ion electrode is the choice technique for the determination of the fluoride content of soft drinks. Using this method, and 0·75 M orthophosphoric acid as a buffer solution, we can determine all the fluoride present in this type of beverage. Besides accuracy and precision, this method offers ease and speed.

However, more complex matrices such as beers offer better results when using potentiometry preceded by heat-facilitated diffusion with prior incineration of the sample, owing to the fact that in this beverage part of the fluoride is present in a combined form. The selective ion electrode is not responsive to this form.

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