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TECHNICAL NOTE

Determination of fluoride in Spanish vinegars

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A simple method for fluoride determination in Spanish vinegars has been developed to provide direct data on dietary fluoride intake from this product. This paper describes a potentiometric method that uses a fluoride selective electrode. Three different TISAB (total ionic strength adjuster buffer) solutions have been evaluated and the method of multiple known additions was used. The precision and accuracy of the developed procedure, in terms of variation coefficient (0·74%) and average percentage of spike recovery (99·9%), are adequate. Forty-two samples of Spanish vinegars were analyzed obtaining a range of fluoride content between 0·12 and 1·95 mg dm^{-3} with an average concentration of 0·52 mg dm^{-3}.

INTRODUCTION

Fluoride content in food is increasing by contamination from: impure phosphate fertilizers, irrigation water with high fluoride levels, fluoridation of drinking water and from excess gas and dust of polluting industries. For this reason, the fluoride content in food is regulated in some countries. In Spain, the majority of the vinegar is derived from wine, and the fluoride content in Spanish vinegars can probably be attributed to the fluoride content of their wines of origin. This anion is naturally found in wine in low concentration, generally not exceeding 1 mg dm^{-3}. Concentration of more than 5 mg dm^{-3} indicates that some form of contamination has taken place.

The fluoride selective electrode is used extensively in food analysis because of its favourable characteristics. The determinations are made in a mixture of the sample solution and a total ionic strength adjuster buffer solution (TISAB solution). The triple function of this conditioning solution is: to eliminate activity problems, to regulate and maintain the pH level, and to complex interfering cations. This is achieved with numerous solutions which combine chelates, salts and buffers in its composition.

In this work, three different TISAB solutions are compared and having selected the optimum one, the concentrations of fluoride in 42 samples of vinegar taken from different markets around Spain were determined. Multiple standard additions was chosen as the analytical measurement technique.

MATERIALS AND METHODS

Apparatus

The following apparatus were used: an Orion model 701 A digital pH/mV meter; an Orion model 94-09 fluoride selective electrode; an Orion model 90-01 single junction reference electrode Ag/KCl (2M)AgCl; an Orion model 90-02 combination pH electrode (Orion Research Inc., Boston, MA, USA). A Selecta model Agitamatic N magnetic stirrer (J. P. Selecta, S. A., Barcelona, Spain) and plastic volumetric material were used when necessary.

Reagents

All chemicals used were Merck analytical-reagent grade or similar. Distilled deionized water was used throughout.

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Stock standard solution: a $1{\cdot}0 \times 10^{-2}$ mol dm^{-3} fluoride solution was prepared from sodium fluoride which had been oven-dried at 120°C for 2 h and stored in a polyethylene bottle. Working standard solutions were prepared by proper dilutions of the stock solution.

TISAB I solution
Hydrochloric acid, 84 cm^3 dm^{-3}; tris (hydroxymethyl) aminomethane, 242 g dm^{-3}; sodium tartrate 2-hydrate, 230 g dm^{-3}. The pH was adjusted to 8·0–8·3.

TISAB II solution
Citric acid, 210 g dm^{-3}; trisodium citrate 2-hydrate, 294 g dm^{-3}; perchloric acid, 42·5 cm^3 dm^{-3}. The pH was adjusted to 5·0–5·5.

TISAB III solution
Supplied by Orion, cat. no. 94-09-11. Contains: acetic acid, ammonium acetate, ammonium chloride and cyclohexylene dinitrilo tetraacetic acid (CDTA). The pH of this solution was 5·3.

Procedure

A vinegar sample (50·0 cm^3) was taken into a plastic beaker, then 4 mol dm^{-3} sodium hydroxide solution (10·0 cm^3) and TISAB III solution (5·0 cm^3) were added. From this solution, 50·0 cm^3 was transferred to another plastic beaker and the fluoride selective and reference electrodes were immersed. Five consecutive additions of 1·0 cm^3 of $1{\cdot}0 \times 10^{-3}$ mol dm^{-3} sodium fluoride were added and the stable potential values (±0·1 mV) were registered. In this potentiometric method, the sample concentration was calculated from the volume of the fluoride solution obtained by extrapolation of the line drawn when potential values versus added volumes of the sodium fluoride solution on a Gran's plot paper (Orion, cat. no. 90-00-90) were plotted, according to the manufacturer's recommendations (Orion Research Inc., 1·970). Finally, the volume of the blank assay was subtracted and the result multiplied by the ratio 65·0 : 50·0.

RESULTS AND DISCUSSION

Because of the acetic acid content in the vinegar, the sample solutions are too acid for direct use of the fluoride ion selective electrode. To avoid using great quantities of TISAB solution, it is necessary to add a basic solution for adjusting the pH value of the vinegar samples near to the value of the TISAB solution. For this reason, potentiometric titrations of some vinegar samples with sodium hydroxide solution were made. From their plots, the volume of sodium hydroxide solution necessary to add to the sample, previous to the addition of TISAB solution, has been determined. This volume was found to be about 10 cm^3 of 4 mol dm^{-3} sodium hydroxide solution.

The minimum volume of each TISAB solution needed to achieve the triple purpose previously mentioned was determined, avoiding an unnecessary dilution of the sample. These volumes were obtained from plots of potential values versus volume of TISAB solution added to a solution which contains 50·0 cm^3 of vinegar sample and 10 cm^3 of a 4 mol dm^{-3} sodium hydroxide solution. The results showed that 8 cm^3 of TISAB I solution, 5 cm^3 of TISAB II solution and 5 cm^3 of TISAB III solution were adequate.

Comparing the different TISAB solutions, the best was selected according to the results of precision and accuracy obtained when the procedure was applied on the same samples of vinegar using the corresponding TISAB solution in each case. The precision was determined by application of the procedure to 11 samples of the same vinegar. After several additions of known concentrations of fluoride ion, the samples were analyzed following the same procedure and the percentages of spike recovery obtained were used to evaluate the accuracy. From data obtained using the three different TISAB solutions, it appears that the best is the TISAB III solution. The results showed an average fluoride content of 0·63 mg dm^{-3} with a standard deviation of $0{\cdot}47 \times 10^{-2}$ mg dm^{-3} and a coefficient of variation of 0·74%, and the percentage of spike recovery ranged from 98·8% to 102·1%.

Forty-two samples of vinegars prepared from red and white wine taken from different Spanish markets were cooled at 8°C in propylene containers. After applying the recommended analytical procedure previously mentioned, the results showed that fluoride concentration ranged from 0·12 to 1·95 mg dm^{-3} with an average value of 0·52 mg dm^{-3}. Although three samples showed very high values, it is possible to state that there is no dispersion of the results obtained since 74% of vinegar samples are included in a concentration range of 0·20–0·80 mg dm^{-3}. If these abnormal data were rejected the average value would be 0·43 mg dm^{-3}.

Unfortunately, the authors could not find any literature on fluoride determination in vinegars and it has thus been impossible to compare the results obtained in this work with other sets of data. On the other hand, if these results are compared with the fluoride contents in wine reported by the authors previous works (Alcorta *et al.*, 1989; Pérez-Olmos *et al.*, 1990), a slight tendency to obtain higher values in vinegars than in wine samples can be observed.

CONCLUSIONS

The use of a fluoride selective electrode in vinegar analysis is a highly attractive possibility because the results obtained have shown that the procedure is simple to operate, precise, reproducible and accurate.

It is possible to ascertain that the contribution of vinegar to total ingestion of fluoride in the alimentary diet is not in itself likely to be dangerous because the fluoride content in vinegar and the quantity of vinegar consumed in the dietary intake is low.

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REFERENCES

Alcorta, J. C., Elias, I., Lima, J. L. F. C. & Pérez-Olmos, R. (1989). Determinacao de fluoretos em vinhos e cervejas com electrodos selectivos de ioes. *Rev. Port. Farm.*, **39**(4), 35–40.

Pérez-Olmos, R., Hardisson, A., Elias, I., Rios, R. & Martin, M. M. (1990). Determination of fluoride in Tenerife wines. Comparative study of conditioning solutions. *Belg. J. Food Chem. Biotechnol.*, **45**(6), 208–13.