ANALYTICAL PROBLEMS IN ASSESSMENT OF FLUORIDE IN FOOD

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SUMMARY: Different conventional digestion methods for the analysis of fluoride in organic material have given ambiguous results. Better, standardised procedures are needed. The present paper discusses some of the fallacies in the analysis of fluoride in solid food, and points out methods to overcome the problems.

Key words: Fluoride analysis; Food; Standard reference material.

INTRODUCTION

Recent concern for the total ingestion of fluoride has brought new emphasis on solid food as a possibly significant fluoride source. Various multidisciplinary researches have provided a vast information on the topic. However, the information is often ambiguous. Our pilot studies on oyster tissue, the only standardised and certified reference material that at the time was available for fluoride analysis, may exemplify the ambiguity. The oyster tissue was dissolved by the use of nitric acid and perchloric acid and the solvent was neutralised with sodium hydroxide and trisodium citrate.[1] According to this method, the fluoride concentration in the oyster tissue is of 24 mg/kg (Table 1). The fluoride concentration given by the producer, National Institute of Standards and Technology (NIST), was 240 mg F/kg. In order to have our findings controlled, oyster samples were sent over to a reference laboratory, which in the first testing, using acid digestion, came up with a fluoride concentration of 2.3 mg/kg. In a second testing, using the ashing method, the fluoride concentration was measured to be 250 mg/kg. Thus, in three analyses we obtained results that differed two orders in magnitude; the ashing method being closest to the value given by NIST.

TABLE 1. Fluoride concentration in oyster tissue (1566a) in mg/kg, as informed and determined by National Institute of Standards and Technology (NIST), using three different methods for digestion of the tissue material. In all cases the fluoride ion-selective electrode was used to determine fluoride in the final solution.

Informative value NIST	Acid digestion method University of Bergen	Acid digestion method Reference laboratory	Ashing method Reference laboratory
240	24	2.3	250

MATERIALS AND METHODS

As the ashing method seamed to give the most reliable results when analysing oyster tissue, we decided to use this method for further studies. In order to evaluate the accuracy of the method, i. e. the agreement between the sample's true content of fluoride and the result of the analysis, we wanted to verify the method through testing of a certified reference material. A reference material or an in-house control material (material prepared in the laboratory) should have a fluoride concentration similar to the concentration expected in the authentic sample. At present, very few reference

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materials certified for fluoride are available. We managed to find four products in addition to the oyster tissue (1566a, from National Institute of Standards and Technology): prawns (GBW 08572), fly ash (GBW 0807) and two brands of maize (GBW 08506, National Research Centre for Certified Reference Materials, China[2]). Unfortunately, both oyster tissue and maize are presently commercially unavailable. We have, consequently, chosen to test two in-house control materials; tea (African Pride, Tanzania Tea Blender LTD., Dar es Salaam, Tanzania) and cod (0271 cod powder, Rieber & Søn A/S, Bergen, Norway), in addition to the prawns.

Dried samples of 0.2 to 2.0 g, depending on the expected fluoride content, were weighed and put into 70 ml nickel crucibles. The samples were covered with 6 ml 8 M sodium hydroxide solution. After the slurries had been evaporated to dryness on a hot plate, the crucibles were covered and combusted in an oven at 525°C. After cooling, distilled water was added and the crucibles were once more put on a hot plate in order to better dissolute the fusion cake. The sample solution was neutralised by nitric acid, TISAB was and the fluoride concentration was measured using an ion selective electrode (Orion 9609) connected to potentiometer (Orion, model 920A).

Linearity of the standard response curve, the limit of determination, the recovery and repeatability were recorded.

RESULTS AND DISCUSSION

Linearity of the standard curve. In Table 2 the r-values from linear regression analysis are given. Satisfactory results were observed with concentrations as low as 0.01 mg F/L and the best results were obtained when using the standards based on blank samples. The r-values describe the linear relationship between mV-readings and fluoride concentration (log F) in the standard solutions. Measuring response was determined using six fluoride concentrations, 0.0001, 0.001, 0.01, 0.1, 1.0 and 10.0 mg F/L covering both sides of the active working range. The standard solutions were prepared by adding sodium fluoride standard (100 mg/L) to blank samples (series 1 and 2 in table 2) or distilled water (series 3 and 4 in Table 2). The reason for using a blank sample to prepare the standards was to obtain the same matrix in the standard solutions as in the samples.

Limit of determination. We tested two different fluoride ion-selective electrodes (A and B) using the same blank solutions. For electrode A, the limit of determination was 0.02 mg F/L, while for electrode B the limit was 0.1 mg F/L. The limit of determination is the lowest amount of fluoride in a sample that can be quantitatively determined with a certain confidence. The limit is calculated as 10 times the standard deviation of the average of the blank samples (N>20). The results illustrate that there can be great differences between electrodes. Electrodes should, therefore, be carefully tested before being used.

Repeatability. In Table 3 the repeatability of three different samples is shown. The relative standard deviation was 8, 13 and 20 % for the oyster tissue, prawns and cod, respectively. This is not satisfactory for the two lowest concentrations. The prawns were certified to 5.31 mg F/kg resulting in a relative error of 9 %. An estimate of the repeatability of a method is obtained when identical test portions are analysed in the same laboratory, using the same equipment and within a short period of time. We

made samples from the same batch, and we used materials ranging over different concentration levels since the precision depends very much on the concentration of the analyte. It should however be noted that the N for oyster tissue and prawns are low and that the analysis of the cod tissue was not obtained in a single day.

TABLE 2. Linear regression analysis of mV-readings vs. log F of 3, 4, 5 or 6 measuring points of the standard curve using fluoride ion-selective electrode. Measuring point 1, 2, 3, 4, 5 and 6 are concentrations of 10, 1.0, 0.1, 0.01, 0.001 and 0.0001 mg F/L, respectively. Series 1 and 2 are made from 100 mg/L NaF-solution diluted in blank samples (NaOH, HCO_3 and distilled water) while series 3 and 4 are diluted to correct concentration with distilled water.

Standards	Series 1 r-values	Series 2 r-values	Series 3 r-values	Series 4 r-values
1, 2, 3, 4, 5 and 6	- 0.9037	- 0.8987	- 0.9112	- 0.9258
1, 2, 3, 4 and 5	- 0.9443	- 0.9420	- 0.9598	- 0.9637
1, 2, 3 and 4	- 0.9812	- 0.9810	- 0.9927	- 0.9907
1, 2 and 3	- 0.9990	- 0.9987	- 0.9999	- 0.9999

TABLE 3. Repeatability of different samples.

Sample type	N	Concentration mg/kg	SD	RSD %	Relative error %
Oyster tissue	5	250	20	8	-
Prawns	4	4.8	0.6	12	9
Cod	26	41	8	20	-

Recovery. In Table 4 the results from the recovery test are shown. We found a recovery of 105 and 95 % in the tea and cod samples, respectively. The recovery is thus within acceptable limits. A known amount of fluoride was added and analysed in order to check the possible interference with the analyte from any compounds in the sample. The amount added should correspond to the level normally present in the sample material and the recovery should be in the range 80-110 %.[3]

TABLE 4. Recovery of fluoride (%) in tea and cod samples.

Tissue	N	g	Added F, µl (100 mg/L)	F in sample mg/kg	Added F mg/kg	Recovery %
Tea	5	0.2000	280	124	238 ± 7	105±7
Cod	5	0.5000	300	37.2	67.6 ± 2.6	95±8

There obviously is need for documentation of the reliability of analytical procedures for the determination of fluoride in foods. To be able to compare results from different studies, analyses that give the total fluoride concentration should be preferred. This is because different acids and different mixtures of acids may dissolve the fluoride in the organic matter to various degrees. The absorption and bioavailability of fluoride from different foods are influenced by several factors e.g. the mineral content of the diet[4,5] and pH of the gastric juices.[6] Therefore it is not possible to extrapolate results obtained by either acid digestion or methods giving the

total fluoride concentration to available fluoride in human beings. Analytical determination of fluoride should preferably be followed up by bioavailability experiments.

There is a great need for a standardised reference material with both low-fluoride and high-fluoride content based on cereals or vegetables. This to have some sort of external test of the methods used. The recovery is often given as a proof for the reliability of a method. A satisfactory recovery tells us that there are no interfering agents and that the fluoride added has been detected. It is important to remember that the recovery tells nothing about how much of the total fluoride in a sample that has been analysed.

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