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Short communication

Determination of fluoride in toothpaste using headspace solid-phase microextraction and gas chromatography–flame ionization detection

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Abstract

A new method for determination of fluoride in toothpaste employing the headspace solid-phase microextraction (HS-SPME) followed by gas chromatography/flame ionization detection (GC/FID) has been proposed. It is a development of the method for determination of fluoride using trimethylchlorosilane (TMCS) as the derivatization reagent to form trimethylfluorosilane (TMFS), with the liquid/liquid extraction (LLE) step replaced by HS-SPME. To introduce the latter, it was necessary to determine the conditions of the reaction and to optimize the two stages of the SPME procedure: extraction and desorption. The parameters of the SPME analysis using carboxen/polydimethylsiloxane (CAR/PDMS) fiber were defined and compared with the corresponding ones for the LLE method, used as a reference. Also, these two methods were compared with respect to their linearity, precision, and accuracy. Results from toothpaste analyses using these two methods were highly correlated, indicating the potential to use the SPME extraction as an inexpensive and solventfree alternative to the LLE method.

Keywords: Fluoride; Gas chromatography; Solid-phase microextraction (SPME); Toothpaste; Trimethylfluorosilane (TMFS)

1. Introduction

Fluoride is a vital ingredient in toothpaste and its quick and reliable determination is important for many purposes. Depending on various factors (e.g., concentration, frequency of use and age of user), fluoride can be detrimental (cause dental fluorosis) or beneficial (prevent tooth decay) [1–3]. This positive effect is obtained with ingredients such as sodium fluoride, sodium monofluorofosfate, stannous fluoride and amine fluoride [4–6].

Several techniques have been used to analyze the water-soluble fluoride species in toothpaste: fluoride ion-selective electrode electroanalysis [7–10], gas chromatography (GC) [11], isotachophoresis [12], ion chromatography (IC) [9,13], flow injection system (FIA) [14] and capillary electrophoresis (CE) [3,5,15]. The most common techniques used are IC and CE. These methods suffer from poor sampling rates and require expensive instrumentation limiting their applicability for routine analyses [15].

Depending on the sample preparation described in these methods, either the total or the soluble or the ionic fluoride content is measured. The prime interest of the formulator and of the manufacturing sites is to control the quantity of fluoride introduced in a given formula, which usually means measuring the total fluoride. The officially recommended method for total fluoride determination described in the Official Journal of the European Communities is based on the derivatization with triethylchlorosilane (TECS) in the presence of hydrochloric acid and subsequent extraction with xylene in the presence of cyclohexane as an internal standard. The procedure published by Cropper and Puttman involved derivatization with trimethylchlorosilane (TMCS), toluene as solvent and *n*-pentane as internal standard [4].

In this method, TMCS was added to the sample solution and the fluoride ions were converted to trimethylfluorsilane (TMFS) through a two-step reaction [11,16].

$$\underset{\text{TMCS}}{(CH_3)_3\text{–Si–Cl}} + H_2O \rightleftharpoons (CH_3)_3\text{–Si–OH} + HCl$$

$$(CH_3)_3\text{–Si–OH} + H^+ + F^- \rightleftharpoons \underset{\text{TMFS}}{(CH_3)_3\text{–Si–F}} + H_2O$$

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TMCS is converted to trimethylsilanol by hydrolysis. Under acidic conditions, trimethylsilanol reacts further with free fluoride ion to form volatile TMFS with a boiling point of 16.4 °C. TMFS is extracted with an organic solvent and then determined quantitatively by gas chromatography [11]. Gas chromatography has also been reported as a suitable method for the determination of trace amounts of fluoride because of its simplicity, accuracy and sensitivity. Its main disadvantage is a rather complicated procedure—fluoride must be converted to TMFS through a two-step reaction and, in addition, TMFS has to be extracted before determination [1].

The conventional extraction method (liquid–liquid extraction), although efficient and precise, are relatively time consuming, hazardous to human health as they use organic solvents and extremely expensive with respect to the disposal of solvents. Therefore, a relatively simple, fast and solvent free extraction method would be desirable. Solid-phase microextraction (SPME) can resolve many of the above problems [17]. SPME is used as a simple and reliable sample preparation technique for the analysis of a variety of organic compounds [18]. It is well known as a method that integrates sampling, extraction, concentration, and sample introduction into a single step. The sample preparation by SPME prior to GC analyses can be more advantageous than conventional solvent extraction [19]. To the best of our knowledge, this method has not been used for the determination of fluoride.

This paper will focus on the optimization and validation of an SPME procedure for the determination of fluoride in toothpaste. The objective of this study was to test the usefulness of the SPME method in the quantitative analysis of fluoride in toothpaste and to compare this low-cost and solventless technique with the liquid–liquid extraction (LLE) method.

2. Experimental

2.1. Reagents and materials

All reagents used were of analytical grade quality or higher. Trimethylchlorosilane was purchased from Sigma–Aldrich (Steinheim, Germany). Sodium fluoride, toluene and hydrochloric acid (35–38%) purchased from POCh (Gliwice, Poland) were used. The internal standard *n*-pentane was obtained from Merck (Darmstandt, Germany). Solid NaF was dried at 105 °C for 2 h prior to the preparation of standard solutions of sodium fluoride. A sodium fluoride stock solution (1 ml = 0.5 mg F^-) was daily prepared by dissolving 0.1105 g of sodium fluoride in 100 ml of double deionized water (in plastic screw-cap tube). Toothpaste containing 0.321% of sodium fluoride was used for optimization studies.

The SPME device (manual fiber holders) and carboxen/polydimethylsiloxane (CAR/PDMS) fibers (75 μm film thickness) were purchased from Supelco (Bellefonte, PA, USA). Before initial use, the fiber was preconditioned in the GC injection port at 300 °C for 2 h.

2.2. GC analysis

The analysis was performed with a HP 5890 Series II gas chromatograph with flame ionization detector (FID) and a split/splitless injection port. The GC system was fitted with a HP-1 column (crosslinked methylsiloxane) 40 m × 0.53 mm I.D., 5 μm film thickness. The gas chromatograph was operated in a splitless mode and the injector port temperature at 200 °C. The splitless time was 4 min. The temperature of FID was 250 °C. The GC oven temperature was programmed as follows: from 80 °C for 0 min to 120 °C at rate of 10 °C/min and then to 220 °C at a rate of 15 °C/min, where it was kept for 2 min. The carrier gas was helium at a constant flow rate of 1.3 ml/min.

2.3. LLE analytical procedure

Eight hundred milligrams of accurately weighed toothpaste, 20 ml of deionized water and 2 ml of hydrochloric acid were introduced into a 60 ml plastic screw-cap tube and mixed for 60 s, followed by addition of 2 ml of TMCS. The mixture was kept on crushed ice for 15 min and then 5 ml of toluene, with *n*-pentane as an internal standard (200 μl of *n*-pentane with 100 ml of toluene), was added for extraction. After shaking for 20 min the tube containing the solution was placed on crushed ice to allow the aqueous-solvent layers to separate. One microliter of the solvent layer was injected into the GC for analysis.

2.4. SPME analytical procedure

Eight hundred milligrams of accurately weighed toothpaste, 30 ml of deionized water and 1 ml of hydrochloric acid were introduced into a 60 ml plastic screw-cap tube (cap with septum) and mixed for 60 s using a vortex mixer. Next, 30 μl of TMCS were added into the tube.

The sample prepared was left for 10 min, where-upon the fiber was placed in the headspace for successive 10 min. During the reaction and extraction, the samples were continuously agitated with a magnetic stir bar on a stir plate at a speed of about 500 rpm. Both stages of the procedure were run at a room temperature of 22 °C. After extraction, the fiber was immediately introduced into the GC injector port for desorption. Thermal desorption of TMFS was carried out for 4 min. After this period no significant blank values were observed.

3. Results and discussion

Studies on the new method for the determination of fluoride in toothpaste were based on the well-known method consisting of a two-stage procedure [4,11,16]. The first stage was derivatization, i.e., preparation of trimethylfluorosilane (TMFS) by the reaction of fluoride with trimethylchlorosilane in an acidic medium. The second stage comprised of a liquid–liquid extraction of the TMFS formed by toluene. Taking advantage of the fact that TMFS is a very volatile compound (Bp 16.4 °C) and the sorption fiber can be placed in the headspace, an attempt was made to replace LLE with the SPME technique as the extraction method.