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Determination of fluoride in toothpaste and in mouthwash products by GC/FID/HS

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Fluorine is imported into the human organism mainly by products for oral hygiene, toothpastes and various liquids for freshening and cleansing the oral cavity. The necessity to control its content is imposed by the requirements for safety and standardized cosmetic products production. The determination was performed by gas chromatography, flame ionization detector and automatic vapor-phase sampler "headspace" (HS). The method was based on derivatization of fluoride anions with triethylchlorsilane (TETCS) in acidic environment. The reaction was realized in the HS vials and after that triethylfluorsilane was determined by gas phase injection. The calibration of the method lies within a concentration interval of 100 – 2000 ppm for toothpaste and 50 - 1000 ppm for mouthwash products. The repeatability, expressed as relative standard deviation at optimized reaction conditions and GC determination was ± 5% for toothpaste and ± 3.5% for mouthwash products. The presented gas-chromatographic method with flame ionization detector and HS appliance enables the quick and precise detection of fluorine in cosmetic products. The method is applicable to various other environments (matrices) – foods, food supplements, drugs.

***Keywords**:* Fluoride; Gas chromatography; Headspace (HS); Toothpaste; Mouthwash products; Triethylfluorosilane (TEFS)

INTRODUCTION

Fluorine is a microelement essential for the organism. It stimulates bone cell formation (osteoblasts), strengthens the skeleton; it is engaged in tooth enamel formation; it has bactericide effect, improves gum blood circulation, prevents caries formation and parodontal diseases in children. On the other hand, excessive fluorine amounts stimulate fluorosis development – it damages the enamel with appearance of red to dark brown stains on it with following defects in the bone tissue; it delays the development of the nervous system that particularly affects growing up organisms and disturbs the processes of ossification and mineralization of the bone tissue.

Various approaches to supply fluorine to various population groups have been implemented in the time over the world. Experiments were conducted (USA) to fluorinate the water for drinking and everyday necessities. Food supplements have been designed, as well as fluorine supplementation of various food products, especially of those, designed for children. Many countries implement fluorine prevention among children through adequate pills. Currently, fluorine delivery to the human organism is mainly realized by products for oral hygiene, toothpastes and various liquids for freshening and cleansing the oral cavity. The implementation of fluorine in toothpastes started in the 60s of the past century substantiated by active scientific research on its effect on human health. The main focus of the studies was oral health with an emphasis on dental caries. The evidence supported fluorine benefits revealing significant reduction of caries incidence rate at application of fluorine-containing toothpastes and liquids for dental hygiene [1, 2].

Practically, the fluorine amount that is necessary and beneficial for the organism varies in very narrow margins and its increase over the upper limit is hazardous.

This fact requires the implementation of a method for control during the production and of the end products that is sensitive, reliable as much as possible, easily applicable and relatively cheap.

Several techniques have been implemented to analyze water soluble fluorides in toothpaste and similar products: fluoride ion selective electrode [3]; ion selective electrode and ion chromatography [4]; capillary electrophoresis [5]. Currently, the most frequently used analytical technique is gas chromatography with flame ionization detector. The gas chromatographic conditions, as well as the chemical reaction when chlorine in triethylchlorsilane is substituted by fluorine in acidic environment are almost equivalent. The new resulting compound triethylfluorsilane can be determined by gas chromatographic method with good analytical parameters. The various developed and published methods contain significant

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differences in the sample preparation before the gas chromatographic determination itself. The standard method set by Directive 83/514 [6] envisages triethylenefluorsilane extraction with a non-polar solvent from the reaction mixture and injection of an aliquot portion into the GC. Wejnerowska *et al.* [7] developed a principally different approach to sample preparation. After the chemical reaction they used an adsorbent instead of a solvent to extract the fluorine compound. The adsorbent was placed in a HS vial and underwent solid-phase headspace micro-extraction and gas chromatography–flame ionization detection.

The aim of the current study was to develop a new efficient, fast and relatively inexpensive method for determination of fluoride in toothpaste and in mouthwash products based on the very rich experience and the high technological levels achieved by the gas chromatography systems.

Reagents and Materials

⇒ *Reagents*: sodium fluoride; triethylchlorosilane – TETCS; sulfuric acid; deionized water (all reagents of quality grade "pure for gas chromatography" or higher).

⇒ *Materials*: various toothpaste brands with/without added fluorine; various mouthwash brands with/without added fluorine.

Gas chromatograph *Clarus 580, Perkin Elmer* with flame ionization detector and automatic vapor phase sampler "headspace" *Turbomatrix HS16*, analytical column Elite CLP 30 m, 25 mm, 0.25µm, vials for HS - 20 mL.

Gas-chromatographic conditions: detector temperature (250ºC), injector (220°C), column (60ºC for 5 min, followed by a raise with 10ºC/min up to 150ºC and 2-min detention); carrier gas helium 20 mL/min.

HS conditions: oven 70ºC; transfer 110ºC; needle 75ºC; carrier gas 28 psi, thermostat 10 min; pressurize time 1.5 min; injection time 0.04 min.

EXPERIMENTAL

Toothpaste

Preparation of basic standards of fluorine: **B 1** - 0.11 g of NaF (0.05g F) in 50 ml of water in a glass flask (0.5 mg/ml) and **B 2** – 1 ml of **B** 1 in 10 ml of water (0.05 mg/ml).

Preparation of laboratory standards: toothpaste without added fluorine, basic composition similar as much as possible to the analyzed one.

The following laboratory standards were prepared: 1 ml B 2 plus 0.5 g paste plus 48.5 ml water; 5 ml B 2 plus 0.5 g paste plus 47.5 ml water; 1 ml B 1 plus 0.5 g paste plus 48.5 ml water; 2 ml B 1 plus 0.5 g paste plus 47.5 ml water. The produced mixtures were homogenized for 30 min in an ultrasound tub.

Preparation of laboratory samples: 0.5 g of the analyzed toothpaste was added to 50 ml of water (glass flask). The mixture was homogenized for 30 min in an ultrasound tub. Three laboratory samples were prepared for each sample.

Of each of the prepared laboratory standards and samples, 1 ml was added into a HS vial plus 1 ml of 50% sulfuric acid and 0.1 ml of triethylchlorsilane (TECS). After adding TECS, the vial must be closed as quickly as possible. The vials were agitated in a shaker at 30°C for 60 min and after that were mounted in the sockets of the HS appliance. Each vial can be injected once.

Mouthwash products

*Preparation of basic standard of fluorine***: B 3**: 1 ml of **B** 1 to 50 ml with mouthwash products without fluorine in a glass flask.

Preparation of laboratory standards in HS vials: 0.1 ml of base 3 plus 0.9 ml of water plus 1 ml of 50% sulfuric acid plus 100 µl of TECS; 0.3 ml of base 3 plus 0.7 ml of water plus 1 ml of 50% sulfuric acid plus 100 µl of TECS; 0.5 ml of base 3 plus 0.5 ml of water plus 1 ml of 50% sulfuric acid plus 100 µl of TECS; 1 ml of base 3 plus 1 ml of 50% sulfuric acid plus 100µl of TECS.

Preparation of laboratory samples: for each analyzed lot two samples were taken. 1 ml of each sample was diluted with 50 ml of mouthwash product without fluorine in a glass flask. Of each of the produced solutions two samples were prepared in headspace vials, respectively: 0.3 ml of sample plus 0.7 ml of water plus 1 ml of 50% sulfuric acid plus 100 µl of TEHS and a similar one, with 0.5 ml of sample. After adding TECS, the vial must be closed as quickly as possible. The vials were agitated for 15 min in a shaker at 30°C and after that they were mounted in the sockets of the HS appliance.

The concentration interval of calibration of the toothpaste was 100 – 2000 ppm, and for mouthwash products - 50 – 1000 ppm. The repeatability, expressed as relative standard deviation at optimized reaction conditions and GC determination, was ± 5% for toothpaste and ± 3.5% for mouthwash products.

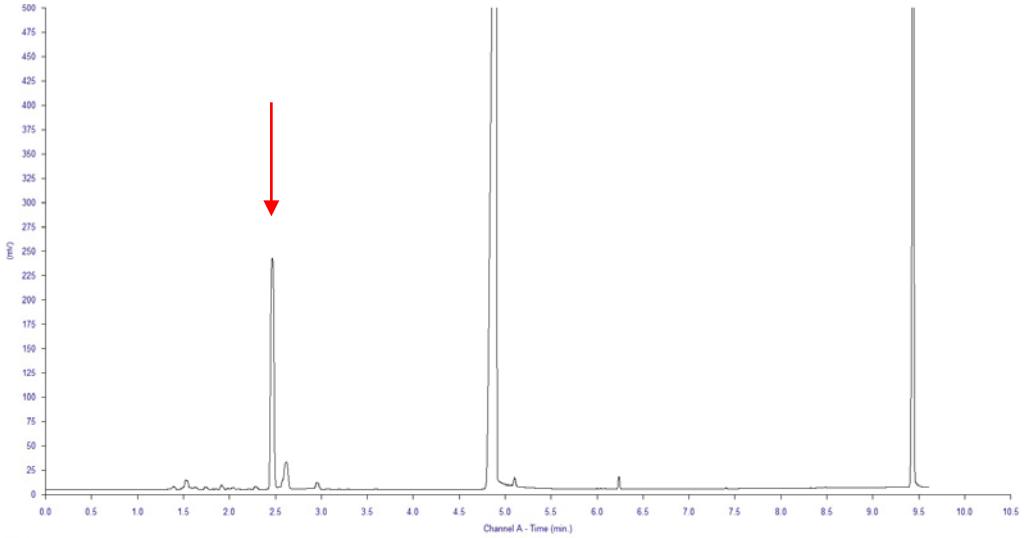

Fig. 1. Chromatogram of a toothpaste with added fluorine (rt = 2.45 min)

The figure 1 presents a chromatogram of a toothpaste sample with added fluorine. The graph clearly outlines the good resolution guaranteeing the achievement of good analytical parameters of the present method.

The method can be applied for various product types, including foods, food supplements, drugs, etc. The optimization of the conditions of the course of the reaction for production of TECS and of the gas chromatographic determination can lead to very high sensitivity at adequate repeatability and absence of systematic error.

CONCLUSION

The proposed gas-chromatographic method with flame ionization detector enables a quick and precise detection of fluorine in cosmetic products. The optimization of the conditions of the course of the reaction for production of TECS and of the gas chromatographic determination can lead to very high sensitivity at adequate repeatability and absence of systematic error. The method can be also applied to other environments (matrices) – foods, food supplements, drugs.

REFERENCES

1. J.D. Featherstone, *J. Amer. Dental Assoc.*, **131**, 887 (2000).
2. V.C.C. Marinho, J.P.T. Higgins, S. Logan, A. Shaiham, Fluoride toothpastes for preventing dental caries in children and adolescents (Cochrane Review). The Cochrane Library, Chichester, UK, John Wiley & Sons Ltd, 2004.
3. Ş. Tokalioğlu, Ş. Kartal, U. Şahin, *J. Chromatogr. A*, **1150,** 173 (2007).
4. T. Itota, T.E. Carrick, S. Rusby, O.T. Al-Naimi, M. Yoshiyama, J.F. McCabe, *J. Dent.* **32**,117 (2004).
5. P. Wang, S.F.Y. Li, H.K. Lee, *J. Chromatogr. A,* **765**, 353 (1997).
6. Directive 83/514/EEC of 27 September 1983 on the approximation of the laws of the Member States relating to methods of analysis necessary for checking the composition of cosmetic products. *Official Journal of the European Communities*, L 291.9, 24.10.1983
7. G. Wejnerowska, A. Karczmarek, J. Gaca, *J. Chromatogr. A*, **1150,** 173 (2007).

ОПРЕДЕЛЯНЕ НА ФЛУОРИД В ПАСТА ЗА ЗЪБИ И ПРОДУКТИ ЗА ОРАЛНА ХИГИЕНА С ИЗПОЛЗВАНЕ НА ГАЗОВА ХРОМАТОГРАФИЯ С ПЛАМЪКОВ ЙОНИЗАЦИОНЕН ДЕТЕКТОР И АВТОМАТИЧНО УСТРОЙСТВО ЗА ВНАСЯНЕ НА ПРОБИ (GC/FID/HS)

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(Резюме)

Флуорът се внася в човешкия организъм главно чрез продукти за орална хигиена, пасти за зъби и различни течности за почистване и освежаване на устата. Необходимостта от контрол на съдържанието му се определя от изискванията за безопасност при производството на козметични продукти. Определянето на флуора е извършено чрез газова хроматография с пламъков йонизационен детектор и автоматично устройство за внасяне на газови проби. Методът се основава на дериватизацията на флуоридните аниони с триетилхлорсилан в кисела среда. Реакцията се провежда в съдчетата на устройството за внасяне на газови проби, след което триетилфлуорсиланът се определя чрез инжектиране на газовата фаза. Калибрирането се извършва в концентрационния интервал 100 – 2000 ppm за пастите за зъби и 50 - 1000 ppm за продуктите за орална хигиена. Повторяемостта, изразена като относително стандартно отклонение, е ± 5% за пастите за зъби и ± 3.5% за продуктите за орална хигиена. Предложеният газ-хроматографски метод с пламъков йонизационен детектор и автоматично устройство за внасяне на газови проби дава възможност за бързо и прецизно определяне на флуор в козметични продукти. Методът е приложим и към различни други матрици – храни, хранителни добавки, лекарства.