

Note

Determination of fluoride and monofluorophosphate in toothpastes by ion chromatography

JEFFREY J. POTTER, AUDREY E. HILLIKER and GEOFFREY J. BREEN*

Central Research Department, Unilever Australia Limited, P.O. Box 9, Balmain, N.S.W. 2041 (Australia)

(First received April 28th, 1986; revised manuscript received June 27th, 1986)

Sodium monofluorophosphate (SMFP) is a therapeutic agent added to toothpastes. Hydrolysis of SMFP during product storage releases free fluoride ions that may subsequently react with other toothpaste ingredients to form insoluble derivatives resulting in loss of active ingredient¹. Quantitative determinations of fluoride and SMFP are important for quality control and stability evaluation of these products.

Gas chromatography², fluoride ion-selective electrode³⁻⁶ and colorimetric⁶ techniques have been used to determine fluorine derivatives in toothpastes. The disadvantage of these methods is that they all measure SMFP indirectly by determining the total fluorine present after acid hydrolysis. Monitoring spontaneous SMFP breakdown requires measurement of free fluoride levels before and after acid hydrolysis.

Additionally, published methods for determination of water-soluble fluoride species in toothpastes²⁻⁸ vary widely in the techniques proposed to produce the aqueous toothpaste extract. In the simplest cases the paste is slurried with cold water and centrifuged^{4,7}; however, others suggest boiling³ or sonicating⁸ the slurry for various times before centrifuging.

Overall, the time consuming sample preparation needed by these methods make them unattractive in quality control applications where many analyses and fast results are required.

Ion chromatographic methods for direct determination of SMFP or free fluoride in toothpastes have been reported^{7,8}. However, to our knowledge, there is no single-column system suitable for the simultaneous determination of fluoride and monofluorophosphate (MFP) ions, particularly in the presence of chloride and sulphate ions that occur in many toothpastes. This paper describes the development of a single-column ion chromatographic method capable of such a determination.

EXPERIMENTAL

Apparatus

The liquid chromatograph consisted of an M-45 pump, a U6K injector and a Model 430 conductivity detector (Waters Assoc., Milford, MA, U.S.A.). The analytical column used was a Waters Assoc. IC-PAK A (50 mm × 4.6 mm I.D.) meth-

acrylate-based anion exchanger (10 μm , 30 $\mu\text{equiv./ml}$). The temperature of the analytical column was maintained with a Waters Assoc. column temperature control system. Chromatographic data were collected and analysed with an HP3350A laboratory automation system (Hewlett-Packard Avondale, PA, U.S.A.). Details of the chromatographic conditions used are listed in Table I.

TABLE I
CHROMATOGRAPHIC CONDITIONS

Eluent flow-rate	1.2 ml/min
Column temperature	35°C
Conductivity detector	
Detector temperature	35°C
Sensitivity	1 μS f.s.d.
Injection volume	20 μl
Recorder chart speed	0.5 cm/min

Reagents

All reagents used were analytical grade, except SMFP (commercial sample, Albright and Wilson, U.K.). SMFP was assayed for purity using the silver precipitation method recommended by the manufacturer.

The internal standard solution (1000 ppm bromide) and the standard fluoride (1000 ppm), chloride (1000 ppm) and SMFP (1.00%) solutions were prepared by dissolving the appropriate amounts of sodium salt in double glass-distilled water.

The eluent, containing 0.6 mM sodium dihydrogen phosphate and 0.4 mM disodium ethylenediaminetetraacetate, was made up in double glass-distilled water. The eluent pH was adjusted to 5.30 with sodium hydroxide solution after degassing by vacuum filtration through a 0.45- μm ME25 membrane filter (Schleicher & Schüll, Dassel, F.R.G.).

Procedure

Calibration. Fluoride calibration solutions were prepared by adding 25–100 μl of fluoride standard solution to 1.0 ml of chloride standard solution and diluting to 25 ml with double glass-distilled water. SMFP calibration solutions were prepared by adding 0.1–0.5 ml of SMFP standard solution to 1.00 ml of bromide standard solution and diluting to 25 ml with double glass-distilled water.

Sample preparation. A 500-mg portion of toothpaste was weighed directly into a 50-ml polypropylene, screw-top test tube. Bromide internal standard solution (1 ml) and double glass-distilled water (24 ml) were added. Two polypropylene rods (25 mm \times 3 mm diameter) were added to aid dispersion and the tube contents mixed using a laboratory vortex mixer at maximum speed for 1 min. A 5-ml aliquot of the dispersion was filtered through a 0.45- μm Millex HV filter unit (Millipore, Bedford, MA, U.S.A.) and passed through a Waters Assoc. Sep-Pak C₁₈ cartridge prior to injection to remove organic components.

with normal toothpaste ingredients. Bromide was also eluted in a chromatographic region free of interference from other toothpaste ion peaks.

The precision of the method was studied for a toothpaste sample containing SMFP as its sole fluoride ingredient. The results of ten separate analyses of this product are shown in Table II. It is interesting to note the appreciable level of fluoride ions present, indicating that spontaneous SMFP hydrolysis had occurred in this product.

REFERENCES

- 1 J. F. de Freitas, *Aust. Dent. J.*, 29 (1984) 30.
- 2 E. Cropper and N. A. Puttnam, *J. Soc. Cosmet. Chem.*, 21 (1970) 533.
- 3 T. S. Light and C. C. Cappuccino, *J. Chem. Educ.*, 52 (1975) 247.
- 4 N. Shane and D. Miele, *J. Pharm. Sci.*, 57 (1968) 1260.
- 5 L. Pickston, *N. Z. J. Technol.*, 1 (1985) 67.
- 6 P. A. Compagnon, *Sci. Tech. Pharm.*, 12 (1983) 495.
- 7 J. S. Fritz, D. L. DuVal, L. Dean and R. E. Barron, *Anal. Chem.*, 56 (1984) 1177.
- 8 S. S. Chen, H. Lulla, F. J. Sena and V. Reynoso, *J. Chromatogr. Sci.*, 23 (1985) 355.