Third Commission Directive 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 (83/514/EEC)

ANNEX

DETERMINATION OF DICHLOROMETHANE AND 1,1,1-TRICHLOROETHANE
DETERMINATION OF TOTAL FLUORINE IN DENTAL CREAMS

1. SCOPE AND FIELD OF APPLICATION

This method is designed for the determination of total fluorine in dental creams. It is suitable for levels not in excess of 0,25 %.

2. DEFINITION

The fluorine content of the sample determined according to this method is expressed as a percentage by mass.

3. PRINCIPLE

The determination is carried out by gas chromatography. The fluorine from the fluorine containing compounds is converted to triethylfluorosilane (TEFS) by direct reaction with chlorotriethylsilane (TECS) in acid solution and simultaneously extracted with xylene containing cyclohexane as internal standard.

4. REAGENTS

All reagents should be of analytical purity.

4.1. Sodium fluoride, dried at 120 ^{o}C to constant mass.

4.2. Water, double distilled or equivalent quality.

4.3. Hydrochloric acid, $d_4^{20} = 1,19$ g/ml.

4.4. Cyclohexane (CH).

4.5. Xylene with no peaks in the chromatogram prior to the solvent peak when chromatographed under the same conditions as the sample (6.1). If necessary purify by distillation (5.8).

4.6. Chlorotriethylsilane (TECS Merck or an equivalent).

4.7. ***Fluorine standard solutions***

4.7.1. Stock solution, 0,250 mg F^{-}/ml. Weigh accurately 138,1 mg of sodium fluoride (4.1) and dissolve in water (4.2). Quantitatively transfer the solution into a 250 ml volumetric flask (5.5). Dilute to the mark with water (4.2) and mix.

4.7.2. Diluted stock solution, 0,050 mg F^{-}/ml. Transfer by pipette 20 ml of the stock solution (4.7.1) into a 100 ml volumetric flask (5.5). Dilute to the mark with water and mix.

4.8. ***Internal standard solution***

Mix 1 ml of cyclohexane (4.4) and 5 ml of xylene (4.5).

4.9. ***Chlorotriethylsilane/internal standard solution***

Transfer, by pipette (5.7), 0,6 ml of TECS (4.6) and 0,12 ml of the internal standard solution (4.8) into a 10 ml volumetric flask. Dilute with xylene (4.5) to the mark and mix. Prepare fresh daily.

4.10. Perchloric acid, 70 % (m/v).

4.11. Perchloric acid, 20 % (m/v) in water (4.2).

5. APPARATUS

5.1. Standard laboratory equipment.

5.2. Gas chromatograph fitted with a flame ionization detector.

5.3. Vortex swirl mixer or equivalent.

5.4. Bühler, shaker, type SMB_1 or equivalent.

5.5. Volumetric flasks, 100 and 250 ml, made of polypropylene.

5.6. Centrifuge tubes (glass); 20 ml with teflon lined screw-caps, Sovirel type 611-56 or equivalent. Clean tubes and screw-caps by leaching several hours in perchloric acid (4.11), followed by five subsequent rinsings with water (4.2), and finally dry at 100 ^{o}C.

5.7. Pipettes, adjustable to deliver volumes of 50 to 200 µl, with disposable plastics tips.

5.8. Distillation apparatus, fitted with a three-ball Schneider column or an equivalent Vigreux column.

6. PROCEDURE

6.1. ***Sample analysis***

6.1.1. Select a dental-cream tube not previously opened, cut open the tube and remove the whole contents. Transfer to a plastics container, mix thoroughly and store under conditions avoiding deterioration.

6.1.2. Weigh accurately 150 mg (m) of sample into a centrifuge tube (5.6), add 5 ml of water (4.2) and homogenize (5.3);

6.1.3. Add 1 ml of xylene (4.5).

6.1.4. Add dropwise 5 ml of hydrochloric acid (4.3) and homogenize (5.3).

6.1.5. Add, by pipette, 0,5 ml of chlorotriethylsilane/internal standard solution (4.9) into the centrifuge tube (5.6).

6.1.6. Close the tube with the screw-cap (5.6) and mix for 45 minutes thoroughly on a shaker (5.4) set at 150 strokes per minute.

6.1.7. Centrifuge 10 minutes at such a speed as to produce a clear separation of the phases, uncap the tube, withdraw the organic layer and inject 3 µl of the organic phase on to the column of the gas chromatograph (5.2).

Remark:

It takes about 20 minutes before all components are eluted.

6.1.8. Repeat the injection, calculate the average peak area ratio (A_{TEFS}/A_{CH}) and read the corresponding amount of fluorine (in milligrams (m_1)) from the calibration graph (6.3).

6.1.9. Calculate the total fluorine content of the sample (in per cent by mass of fluorine) as indicated in paragraph 7.

6.2. ***Chromatographic conditions***

6.2.1. Column: stainless steel.

Length: 1,8 m.

Diameter: 3 mm.

Support: Gaschrom Q 80 to 100 mesh.

Stationary phase: silicon oil DC 200 or equivalent, 20 %. Condition the column overnight at 100 °C (carrier gas flow at 25 ml nitrogen per minute) and repeat every night. After each fourth or fifth injection recondition the column by heating for 30 minutes at 100 °C.

Temperatures:

column	:	70 °C,
injector	:	150 °C,
detector	:	250 °C.

Gas flow carrier: 35 ml of nitrogen per minute.

6.3. ***Calibration graph***

6.3.1. Place, by pipette, into a series of six centrifuge tubes (5.6), 0, 1, 2, 3, 4 and 5 ml of the diluted fluoride standard solution (4.7.2). Make up the volume in each tube to 5 ml with water (4.2).

6.3.2. Proceed as described under 6.1.3 to 6.1.6 inclusive.

6.3.3. Inject 3 µl of the organic phase on to the column of the gas chromatograph (5.2).

6.3.4. Repeat the injection and calculate the average peak ratio (ATEFS/ACH).

6.3.5. Plot a calibration graph correlating the mass of fluorine (in milligrams) in the standard solutions (6.3.1) and the peak area ratio (ATEFS/ACH) measured under 6.3.4. Connect the points of the graph with the best fitting straight line calculated by regression analysis.

7. CALCULATION

The concentration of the total fluorine content of the sample (in per cent by mass of fluorine) (% (m/m) F) is given by:

$$\% \, F = \frac{m_1}{m} \times 100 \, \%$$

where:

m	=	the test portion (in milligrams) (6.1.2),
m_1	=	the amount of F (in milligrams) read from the calibration graph (6.1.8).

8. REPEATABILITY[1]

For a fluorine content of about 0,15 % (m/m), the difference between the results of two determinations carried out in parallel on the same sample should not exceed an absolute value of 0,012 % (m/m).

(**1**) Norm ISO 5725.