II

(Acts whose publication is not obligatory)

COMMISSION

FIFTH COMMISSION DIRECTIVE 93/73/EEC

of 9 September 1993

on the methods of analysis necessary for checking composition of cosmetic products

THE COMMISSION OF THE EUROPEAN COMMUNITIES,

Having regard to the Treaty establishing the European Economic Community,

Having regard to Council Directive 76/768/EEC of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products (1), as last amended by Directive 93/35/EEC (2), and in particular Article 8 (1) thereof,

Whereas Directive 76/768/EEC provides for the official testing of cosmetic products with the aim of ensuring that the conditions laid down by Community provisions concerning the composition of cosmetic products are satisfied;

Whereas all the necessary methods of analysis should be laid down as quickly as possible; whereas four steps have already been taken by Commission Directive 80/1335/EEC (3), as amended by Directive 87/143/EEC (4), Commission Directive 82/434/EEC (5), as amended by Directive 90/207/EEC (6) and Commission Directives 83/514/EEC (7) and 85/490/EEC (8); whereas the identification and determination of silver nitrate, the identification and determination of silver nitrate, the identification and determination of selenium disulphide in anti-dandruff shampoos, the determination of soluble barium and soluble strontium in pigments in the form of salts or lakes, the identification and determination of benzyl alcohol, the identification of zirconium, and the determination of zirconium, aluminium and chlorine in non-aerosol antiperspirants and the identification and determination of hexamidine, dibromohexamidine, dibromopropamidine and chlorhexidine, constitute a fifth step;

Whereas the measures provided for in this Directive are in accordance with the opinion of the Committee on the adaptation of Directive 76/768/EEC to technical progress,

HAS ADOPTED THIS DIRECTIVE:

Article 1

Member States shall take all necessary steps to ensure that during official testing of cosmetic products, the:

— identification and determination of silver nitrate,

— identification and determination of selenium disulphide in anti-dandruff shampoos,

— determination of soluble barium and soluble strontium in pigments in the form of salts or lakes,

— identification and determination of benzyl alcohol,

— identification of zirconium, and determination of zirconium, aluminium and chlorine in non-aerosol antiperspirants,

— identification and determination of hexamidine, dibromohexamidine, dibromopropamidine and chlorhexidine,

shall be carried out in accordance with the methods described in the Annex.

(1) OJ No L 262, 27. 9. 1976, p. 169.
(2) OJ No L 151, 23. 6. 1993, p. 32.
(3) OJ No L 383, 31. 12. 1980, p. 27.
(4) OJ No L 57, 27. 2. 1987, p. 56.
(5) OJ No L 185, 30. 6. 1982, p. 1.
(6) OJ No L 108, 28. 4. 1990, p. 92.
(7) OJ No L 291, 24. 10. 1983, p. 9.
(8) OJ No L 295, 7. 11. 1985, p. 30.

Article 2

1. Member States shall bring into force the laws, regulations or administrative provisions needed to comply with this Directive no later than 30 September 1994. The shall forthwith inform the Commission thereof.

When Member States adopt these provisions, these shall contain a reference to this Directive or shall be accompanied by such reference at the time of their official publication. The procedure for such reference shall be adopted by Member States.

2. Member States shall communicate to the Commission the provisions of national law which they adopt in the field covered by this Directive.

Article 3

This Directive is addressed to the Member States

Done at Brussels, 9 September 1993.

For the Commission

Christiane SCRIVENER

Member of the Commission

ANNEX

IDENTIFICATION AND DETERMINATION OF SILVER NITRATE IN COSMETIC PRODUCTS

A. Identification

1. *Scope and field of application*

This method describes the identification of silver nitrate as silver in aqueous cosmetic products.

2. *Principle*

Silver is identified by the characteristic white precipitate formed with chloride ions.

3. *Reagents*

All reagents must be of analytical purity.

3.1. Hydrochloric acid solution, 2 M

3.2. Ammonia solution : dilute concentrated ammonium hydroxide solution (d_{20} = 0,88 g/ml) with an equal quantity of water and mix.

3.3. Nitric acid solution, 2 M

4. *Apparatus*

4.1. Normal laboratory equipment

4.2. Centrifuge

5. *Procedure*

5.1. To about 1 g of sample in a centrifuge tube add 2 M hydrochloric acid solution (3.1) dropwise until precipitation is complete ; mix and centrifuge.

5.2. Discard the supernatant liquid and wash the precipitate once with five drops of cold water. Reject the washings.

5.3. Add a quantity of water equal to the bulk of precipitate in the centrifuge tube. Heat to boiling and stir.

5.4. Centrifuge hot ; discard the supernatant liquid.

5.5. To the precipitate add a few drops of ammonia solution (3.2) ; mix and centrifuge.

5.6. To one drop of the supernatant liquid on a glass slide add a few drops of 2 M nitric acid solution (3.3).

5.7. A white precipitate indicates the presence of silver.

B. Determination

1. *Scope and field of application*

This method is suitable for the determination of silver nitrate as silver in cosmetic products intended to dye eyelashes or eyebrows.

2. *Principle*

Silver is determined in the product by atomic absorption spectrometry.

3. *Reagents*

All reagents must be of analytical purity.

3.1. Nitric acid solution, 0,02 M

3.2. Silver standard solutions

3.2.1. Stock silver standard solution, 1 000 µg/ml in 0,5 M nitric acid solution ('SpectrosoL' or equivalent)

3.2.2. Silver standard solution, 100 µg/ml : transfer by pipette 10 ml of the stock silver standard solution (3.2.1) into a 100-ml volumetric flask. Make up to volume with 0,02 M nitric acid solution (3.1) and mix. This standard solution should be freshly prepared and stored in a dark-coloured glass bottle

4. *Apparatus*

4.1. Normal laboratory equipment

4.2. Atomic absorption spectrophotometer equipped with a silver hollow-cathode lamp

5. *Procedure*

5.1. Sample preparation

Weigh accurately approximately 0,1 g (m gram) of an homogenous sample of the product. Transfer quantitatively into a one-litre volumetric flask and make up to volume with 0,02 M nitric acid solution (3.1) and mix.

5.2. Conditions for atomic absorption spectrometry

Flame : air-acetylene

Wavelength : 338,3 nm

Background correction : yes

Fuel condition : lean ; for maximum absorbance, optimization of burner height and fuel conditions will be necessary.

5.3. Calibration

5.3.1. Into a series of 100-ml volumetric flasks transfer by pipette 1,0, 2,0, 3,0, 4,0 and 5,0 ml of the silver standard solution (3.2.2). Make up each flask to volume with 0,02 M nitric acid solution (3.1) and mix. These solutions contain 1,0, 2,0, 3,0, 4,0 and 5,0 µg silver per millilitre, respectively.

5.3.2. Measure the absorbance of a 0,02 M nitric acid solution (3.1) and use the value obtained as the zero silver concentration for the calibration curve. Measure the absorbance of each silver calibration standard (5.3.1). Plot a calibration curve relating absorbance values to silver concentration.

5.4. Determination

Measure the absorbance of the sample solution (5.1). From the calibration curve read off the concentration of silver corresponding to the absorbance value obtained for the sample solution.

6. *Calculation*

Calculate the silver nitrate content of the sample, in percentage by mass (% m/m), using the formula :

$$\%\ (m/m)\ \text{of silver nitrate} = \frac{1{,}5748 \times c}{10 \times m}$$

in which :

m = mass in grams of the sample taken for analysis (5.1) ;

and

c = concentration of silver in the sample solution (5.1), in micrograms per millilitre, obtained from the calibration curve.

7. *Repeatability*(1)

For a silver nitrate content of 4 % (m/m) the difference between the results of two determinations carried out in parallel on the same sample should not exceed 0,05 % (m/m).

IDENTIFICATION AND DETERMINATION OF SELENIUM DISULPHIDE IN ANTI-DANDRUFF SHAMPOOS

A. Identification

1. *Scope and field of application*

This method describes the identification of selenium disulphide as selenium in anti-dandruff shampoos.

2. *Principle*

Selenium is identified by the characteristic yellow to orange colour produced on reaction with urea and potassium iodide.

(1) ISO 5725.

3. *Reagents*

All reagents must be of analytical purity.

3.1. Nitric acid, concentrated (d_{20} = 1,42 g/ml)

3.2. Urea

3.3. Potassium iodide solution, 10 % (m/v): dissolve 10 g of potassium iodide in 100 ml of water

4. *Apparatus*

4.1. Normal laboratory equipment

4.2. Digestion tube, 100-ml capacity

4.3. Heated-block digestor

4.4. Filter paper (Whatman No 42 or equivalent) or a 0,45 µm membrane filter

5. *Procedure*

5.1. To approximately 1 g of shampoo in a digestion tube (4.2) add 2,5 ml of concentrated nitric acid (3.1) and digest at 150° C for 30 minutes on a heated-block digestor (4.3).

5.2. Dilute the digested sample to 25 ml with water and filter through a filter paper or a 0,45 µm membrane filter (4.4).

5.3. To 2,5 ml of the filtrate add 5 ml water, 2,5 g urea (3.2) and boil. Cool and add 1 ml of potassium iodide solution (3.3).

5.4. A yellow to orange colour which darkens rapidly on standing indicates the presence of selenium.

B. Determination

1. *Scope and field of application*

This method is suitable for the determination of selenium disulphide as selenium in anti-dandruff shampoos containing up to 4,5 % (m/m) selenium disulphide.

2. *Principle*

The sample is digested with nitric acid and the selenium in the resultant digest determined by means of atomic absorption spectrometry.

3. *Reagents*

All reagents must be of analytical purity.

3.1. Nitric acid, concentrated (d_{20} = 1,42 g/ml)

3.2. Nitric acid solution, 5 % (v/v): add 50 ml concentrated nitric acid (3.1) to 500 ml of water in a beaker, stirring continuously. Transfer this solution to a one-litre volumetric flask and make up to volume with water.

3.3. Stock selenium standard solution, 1 000 µg/ml in 0,5 M nitric acid solution ('SpectrosoL' or equivalent)

4. *Apparatus*

4.1. Normal laboratory equipment

4.2. Digestion tube, 100-ml capacity

4.3. Heated-block digestor

4.4. Filter paper (Whatman No 42 or equivalent) or a 0,45 µm membrane filter

4.5. Atomic absorption spectrophotometer equipped with a selenium hollow-cathode lamp