SLOVENSKI STANDARD
oSIST prEN 16342:2012

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Kozmetika - Analiza kozmetičnih izdelkov - Kvantitativno določevanje cinkovega piritiona, pirokton olamina in klimbazola v kozmetičnih izdelkih

Cosmetics - Analysis of cosmetic products - Quantitative determination of zinc pyrithione, piroctone olamine and climbazole in cosmetic products

Kosmetische Mittel - Untersuchung von kosmetischen Mitteln - Quantitative Bestimmung von Zinkpyrithion, Pirocton-Olamin und Climbazol in tensidhaltigen kosmetischen Mitteln mit Antischuppenwirkstoffen

Cosmétiques - Détermination quantitative du zinc pyrithione, de la piroctone olamine et du climbazole dans les produits cosmétiques

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Cosmetics - Analysis of cosmetic products - Quantitative determination of zinc pyrithione, piroctone olamine and climbazole in cosmetic products

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (prEN 16342:2011) has been prepared by Technical Committee CEN/TC 392 “Cosmetics”, the secretariat of which is held by AFNOR.

This document is currently submitted to the CEN Enquiry.

Introduction

Special hair products contain substances to help prevent dandruff. These substances mainly inhibit the development of microorganisms, which often are the cause of dandruff. The most commonly used substances are zinc pyrithione, piroctone olamine and climbazole. The substances are regulated by Council Directive of 27 July 1976 on the approximation of the laws of the member states relating to cosmetic products (EC 76/768/EEC) as well as Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products. Limits for these substances are listed in the annexes regulating preservatives in cosmetic products. Zinc pyrithione is additionally listed in Annex III of both regulative documents named above.

NOTE As the Regulation (EC) 1223/2009 applies in total from 11 July 2013 and replaces Directive 76/768/EEC the following details relate only to Regulation (EC) 1223/2009.

Reference Number, maximum authorized concentration in hair products, limitations and requirements:

Annex III Regulation (EC) 1223/2009

Zinc pyrithione:	No. 101:	0,1 % leave-on hair products	Remark: For purposes other than inhibiting the development of microorganisms in the product. This purpose has to be apparent from the presentation of the product.

Annex V Regulation (EC) 1223/2009

Zinc pyrithione:	No. 8:	1,0 % hair products	Remark: Only in rinse-off products
		0,5 % other products	Remark: Not to be used in oral products

Climbazole:	No. 32:	0,5 %	
Piroctone olamine:	No. 35:	1,0 % rinse-off products	
		0,5 % other products	

1 Scope

This draft standard describes an analytical method for the detection and quantitative determination of the following anti-dandruff agents: Zinc pyrithione, piroctone olamine and climbazole in surfactant-containing cosmetic products in the concentration range from 0,1 g/100 g to 1,0 g/100 g.

NOTE The method is also suitable for the determination of ketoconazole and ciclopirox olamine (q.v. Annex A) in surfactant-containing cosmetic products and it's probably applicable for the determination of the substances in non surfactant-containing cosmetic products. For these purposes the method has not been validated.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
anti-dandruff agents
substances, added to hair care products, active against the development of microorganism e.g. zinc pyrithione, piroctone olamine and climbazole

3 Principle

The anti-dandruff agents are extracted from the cosmetic sample matrix using dichloromethane and methanol. Each analyte present in the sample extract is separated using reversed phase HPLC with UV (DAD) detection. The quantitative determination is made using the external standard method of calibration.

4 Reagents

4.1 General

If not otherwise specified, minimum analytical-grade chemicals shall be used; water shall be distilled or of a corresponding purity. "Solution" shall be understood as an aqueous solution unless otherwise specified.

4.2 Methanol, CAS number 67-56-1

4.3 Dichloromethane, CAS number 75-09-02

4.4 Acetonitrile, CAS number 75-05-8

4.5 Ethylenediaminetetraacetic acid (EDTA) disodium salt dihydrate ($Na_2EDTA \times 2H_2O$), CAS number 6381-92-6

4.6 Oxalic acid dehydrate CAS number 6153-56-6

4.7 Acetic acid (glacial), CAS number 64-19-7, mass fraction w = 99,8 g/100 g

4.8 Acetic acid, molar concentration c = 0,02 mol/l

Weigh 1,20 g of acetic acid glacial (4.7) into a 1 l volumetric flask and fill with water up to the calibration mark.

4.9 Methanol/acetic acid mixture

Mix 80 parts by volume of methanol (4.2) and 20 parts by volume of acetic acid (4.8).

4.10 Sodium hydroxide solution, molar concentration c = 1 mol/l

4.11 Eluents

4.11.1 Eluent A: 0,0027 mol/l of oxalic acid dihydrate (4.6) and 0,001 mol/l of EDTA (4.5) in water, pH 4,0:

Pre-dissolve 0,37 g of EDTA in water, add 0,35 g of oxalic acid dihydrate (0,025 % of oxalic acid) and adjust to pH = 4,0 with sodium hydroxide solution (4.10) using a pH-Meter. Then fill with water up to the 1000 ml mark.

4.11.2 Eluent B: Acetonitrile (4.4)

4.12 Reference substances

For the reference substances no purity is defined. However the purity of the reference substances must be known to determine the definite amount of standard in the calibration solution.

4.12.1 Zinc pyrithione, CAS number 13463-41-7

4.12.2 Piroctone olamine
(1-hydroxy-4-methyl-6-(2,4,4-trimethylpentyl)-2-pyridone), CAS number 68890-66-4

4.12.3 Climbazole
(1-(4-chlorophenoxy)-1-(imidazol-1-yl)-3,3-dimethyl-2-butanone), CAS number 38083-17-9

4.13 Stock solutions

4.13.1 General

Fresh stock solutions need to be prepared each working day.

4.13.2 Zinc pyrithione stock solution, mass concentration β = 250 mg/l

Weigh approximately 25 mg of zinc pyrithione (4.12.1) to the nearest 0,1 mg into a 100 ml volumetric flask, dissolve in 50 ml of dichloromethane (4.3) and fill up to the mark with the methanol/acetic acid mixture (4.9).

4.13.3 Piroctone olamine and climbazole stock solution, mass concentration β = 250 mg/l

Weigh approximately 25 mg of each piroctone olamine (4.12.2) and climbazole (4.12.3) to the nearest 0,1 mg into a 100 ml volumetric flask and fill up to the mark with the methanol/acetic acid mixture (4.9).

4.14 Calibration solutions

Fresh calibration solutions shall be prepared each working day.

The following scheme in table 1 for the preparation of the calibration solutions has proved useful in practice:

Together, the given amounts of the stock solutions in ml, are pipetted into 25 ml volumetric flask and filled up to the mark with the methanol/acetic acid mixture (4.9).

For calculation the concentration of the calibration solutions have to be corrected with the known purity of the reference substances.

Table 1 — Calibration solution

Calibration solution	Zinc pyrithione (4.13.2) ml	Piroctone olamine + Climbazole (4.13.3) ml	Concentration µg/ml
1	0,5	0,5	5
2	1	1	10
3	2	2	20
4	3	3	30
5	5	5	50

5 Apparatus and equipment

5.1 Analytical balance with a precision of 0,1 mg

5.2 Membrane filter for solvent filtration, 0,45 µm pore size

5.3 Ultrasonic bath with temperature controlled heater

5.4 Disposable syringes

5.5 Membrane filter for sample filtration, e.g. PTFE, 0,45 µm pore size

5.6 High-performance liquid chromatograph consisting of:

— sampling device;

— pump system with gradient function;

— degasser (optionally; eluent may be degassed prior to use if the system requirements are fulfilled (s.a.));

— column oven;

— photodiode array detector (for quantitative determination without Identification a multiple wavelength detector is sufficient);

— evaluation system.

5.7 Analytical reversed-phase separation column, e.g.:

Onyx Monolithic C18 100 mm × 3 mm (Fa. Phenomenex) or Chromolith RP18e, 100 mm × 3 mm (Fa. Merck).

A pre-column packed with stationary phase similar to the analytical separation column shall be used.

6 Sampling

The sampling technique is not part of the technique specified in the official method.

7 Procedure

7.1 Sample preparation

Weigh approximately 250 mg of sample to the nearest 0,1 mg into a 50 ml volumetric flask. Add 5 ml of dichloromethane (4.3) and 5 ml of methanol (4.2). Place the volumetric flask into a temperature controlled ultrasonic bath for 10 min and heat gently at 35 °C to 40 °C. Allow the sample to dissolve or homogeneously disperse and let the sample cool down at room temperature. Fill the volumetric flask to the mark with methanol/acetic acid (4.9) and shake. Filter approximately 2 ml of methanol/acetic acid mixture through a membrane filter (5.5) into a HPLC vial, discarding the first 0,5 ml.
Fresh sample solutions shall be prepared each working day.

7.2 High-performance liquid chromatography (HPLC)

When starting measurements, examine the baseline stability and response linearity of the detector. The detector shall be able to detect the lowest calibration solution of climbazole (5µg/ml) at a signal to noise ratio of 6:1. The same operating conditions of the HPLC System shall be maintained throughout the measurements of all sample and calibration solutions.

When using the apparatus (5.6) and the column of (5.7), the following conditions have shown useful:

- flow: 2,0 ml/min
- injection volume: 5 µl
- injector temperature: room temperature
- column temperature: 30 °C
- detection: Zinc pyrithione: detection wavelength:λ = 340 nm
  Climbazole: detection wavelength: λ = 277 nm
  Piroctone olamine: detection wavelength: λ = 305 nm
- running time: 6 min

Gradient elution

Eluent A: 2,7 mol/m^3 of oxalic acid + 1 mol/m^3 of EDTA in water, pH 4,0 (4.11)

Eluent B: Acetonitrile (4.4)

For the gradient elution eluents A and B are used in accordance with the volume ratios and time intervals given in the table below, the following conditions have proved useful: