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**Kozmetika - Analiza kozmetičnih izdelkov - Kvantitativno določevanje cinkovega piritiona, pirokton olamina in klmbazola v kozmetičnih izdelkih proti prhljaju, ki vsebujejo površinsko aktivne snovi**

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

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

Cosmétiques - Analyse des produits cosmétiques - Détermination quantitative de la pyrithione de zinc, de la piroctone olamine et du climbazole dans les produits cosmétiques antipelliculaires contenant des agents de surface

**Ta slovenski standard je istoveten z: EN 16342:2013**

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**en,fr,de**

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EUROPEAN STANDARD

**EN 16342**

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English Version

## Cosmetics - Analysis of cosmetic products - Quantitative determination of zinc pyrithione, piroctone olamine and climbazole in surfactant containing cosmetic anti-dandruff products

Cosmétiques - Analyse des produits cosmétiques - Détermination quantitative de la pyrithione de zinc, de la piroctone olamine et du climbazole dans les produits cosmétiques antipelliculaires contenant des agents de surface

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

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## Foreword

This document (EN 16342:2013) has been prepared by Technical Committee CEN/TC 392 “Cosmetics”, the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2013, and conflicting national standards shall be withdrawn at the latest by November 2013.

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## 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 authorised 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.
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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

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

## 1 Scope

This European Standard specifies 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 is 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 term and definition applies.

### 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

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### 4.1 General

If not otherwise specified, as a 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<sub>2</sub>EDTA · 2H<sub>2</sub>O)**, CAS number: 6381-92-6.

**4.6 Oxalic acid dihydrate**, 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).

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**4.10 Sodium hydroxide solution**, molar concentration  $c = 1 \text{ mol/l}$ .

**4.11 Eluents**

**4.11.1 Eluent A:** 0,002 7 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****4.12.1 General**

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

**4.12.2 Zinc pyrithione**, CAS number: 13463-41-7.

**4.12.3 Piroctone olamine**, (1-(4-chlorophenoxy)-1-(imidazol-1-yl)-3,3-dimethyl-2-butanone), CAS number: 68890-66-4.

**4.12.4 Climbazole**, (1-(4-chlorophenoxy)-1-(imidazol-1-yl)-3,3-dimethyl-2-butanone), CAS number: 38083-17-9.

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**4.13 Stock solutions****4.13.1 General**

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Fresh stock solutions need to be prepared each working day.

**4.13.2 Zinc pyrithione stock solution**, mass concentration  $\beta = 250 \text{ mg/l}$ .

Weigh approximately 25 mg of zinc pyrithione (4.12.2) 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  $\beta = 250 \text{ mg/l}$ .

Weigh approximately 25 mg of each piroctone olamine (4.12.3) and climbazole (4.12.4) 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 pyriothione (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 (q.v.));
- 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 (Phenomenex)<sup>1)</sup> or Chromolith RP18e, 100 mm × 3 mm (Merck)<sup>1)</sup>.

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 standard method.

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1) This is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by CEN of this product. Equivalent products may be used if they can be shown to lead to the same results.