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Cosmetics — Analytical method — Detection and quantitative determination of Diethanolamine (DEA) by GC/MS

Cosmétique — Méthode analytique — Détection et dosage quantitatif de la diéthanolamine (DEA) par CG/SM

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 217, *Cosmetics*.

Introduction

Diethanolamine (DEA) has been restricted for use in cosmetics and personal care products in a number of jurisdictions due to its potential health risk since residual levels of DEA might react with other specific ingredients to form the extremely potent carcinogen nitrosodiethanolamine (NDELA). Therefore, a harmonized method for the screening of DEA in cosmetic raw materials is considered important.

Numerous methods for the trace analysis of alkanolamines including DEA in different sample matrices have been developed and published[1] [2] [3]. Among the methods available for the analysis of alkanolamines, techniques using gas chromatography (GC) or liquid chromatography (LC) with a variety of detector systems have received the most attention[4] [5]. More recent procedures, mass spectrometry (MS) detection in combination with chromatography separation is used to determine analyte content in aqueous solutions with minimal requirements for extraction and cleanup.[6] [7] In some cases, derivatization of alkanolamines has also been used to improve the chromatographic separations and detection[8] [9].

This document describes a rapid and simple method suitable for simultaneously qualitative and quantitative screening of cosmetics and cosmetic raw materials containing residue of above 0,1 % diethanolamine (DEA).

Cosmetics — Analytical method — Detection and quantitative determination of Diethanolamine (DEA) by GC/MS

1 Scope

This document describes a screening method for rapid sampling and identifying of diethanolamine (DEA) in cosmetics and raw materials used in cosmetics by gas chromatography – mass spectroscopy (GC-MS).

This method is not applicable to the detection and/or quantification of DEA-related ingredients. When this method is used to analyse unfamiliar sample matrices analysts are advised to confirm the applicability and flexibility of the techniques in their matrix.

Under the conditions specified this method is reliable for quantification with DEA level at 1 000 mg/kg (0,1 %).

However, samples with lower concentrations (<0,1 %) or otherwise unusual compositions or characteristics can present difficulties (such as, for example, peak tailing) that preclude the direct use of this method.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at http://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Principle

The analyte is extracted with anhydrous ethanol from the sample matrix by ultrasonic extraction. Following ultrasonic treatment, the extract is separated from non-soluble compounds by centrifugation treated with anhydrous sodium sulfate (Na_2SO_4), and filtered. The extract thus obtained is then ready for final identification and the quantification with GC-MS. Qualitative results are based on retention timeand confirmed by mass spectrometry. A calibration curve prepared from external standards is then used for quantitative analysis.

5 Procedure

5.1 Preparation of calibration solutions

5.1.1 Stock solution

A DEA stock solution (5 000 µg/ml) is prepared by weighing accurately about 0,5 g of DEA in a 100 ml volumetric flask), dissolving it in ethanol and diluting to the mark. Transfer the stock standard solution into a polytetrafluoroethylene (PTFE)-sealed screw-cap bottle and store in a dark place at a temperature of about 4 °C.

Alternatively, stock solution of DEA may be purchased as certified solutions.

5.1.2 Standard solution

Prepare one intermediate standard solution of 1 000 µg/ml by pipetting 20 ml of stock solution (5.1.1) to a 100 ml volumetric flask and diluting to the mark with ethanol. Transfer the standard solution into a polytetrafluoroethylene (PTFE)-sealed screw-cap bottle and store in a dark place at a temperature of about 4 °C.

Standard solutions are stable for 2 w but should be checked regularly for signs of degradation or evaporation and again just prior to preparing calibration standards from them.

5.1.3 Calibration solutions

Prepare calibration solutions by successive dilutions of the standard solution (5.1.2) according to Table 1. Transfer 5,0 ml, 4,0 ml, 3,0 ml, 2,0 ml, 1,0 ml or 0,5 ml of the stock standard solution to a series of 10 ml volumetric flasks and bring up to reference level with ethanol. These solutions contain, respectively, 500 µg/l, 400 µg/ml, 300 µg/ml, 200 µg/ml, 100 µg/ml or 50 µg/ml DEA in ethanol. Transfer the calibration solutions into polytetrafluoroethylene (PTFE)-sealed screw-cap bottles and store in a dark place at a temperature of about 4 °C.

Table 1 — Preparation of calibration solutions

Calibration solutions	C1	C2	C3	C4	C5	C6	C7
Volume of the standard solution added/ml	0	0,5	1,0	2,0	3,0	4,0	5,0
Final volume/ml	10	10	10	10	10	10	10
The approximate concentration of DEA[a]/(µg/ml)	0	50	100	200	300	400	500
NOTE Calibration solutions are stable for 1 w.							
[a] The precise concentration of DEA is obtained by the calculation with the mass of DEA.							

5.2 Sample preparation

Weigh accurately about 1,0 g of the sample to a 10 ml volumetric flask. Add 5,0 ml ethanol and extract for approximately 15 min using ultrasonic treatment. Then bring the total volume to 10 ml with ethanol and centrifuge at 6 000 r/min for 10 min. Take the supernatant in a fresh tube, add 1,5 g of anhydrous sodium sulfate, and filter the collected solution through a 0,45 µm filter membrane into a vial for analysis.

5.3 Analysis

5.3.1 General

The samples, including the quality control samples, are analysed by GC-MS.

5.3.2 Example of instrumental conditions

— Injection volume: 1 µl, split injection, split ratio 30:1

— Column: 6 % cyanopropylphenyl stationary phase column such as Agilent J&W DB-624[1)] (30m × 0,25 mm ID, film thickness 1,40 µm), RESTEK (Rx®-5 ms, 30 m, 0,25 mm ID, 0,25 µm)[2)] or another type suited for the purpose.

— Column temperature: 30 °C/min up to 200 °C (hold 5 min) from 80 °C (hold 5 min), 50 °C/min up to 260 °C (hold 2 min).

— Injector: 250 °C

— Carrier gas: helium, about 1 ml/min

— Source temp: 180 °C

— Transfer line: 250 °C

— Electron energy: 70 eV

— EI MS scan mode: 28 amu to 300 amu

Monitoring ions (*m/z*) are shown in Table 2.

Table 2 — DEA selected ions

Detect ion (*m/z*)	Relative Intensity (% of base peak)
74	100
56	50
45	15
30	25

As a reference example, see Annex A.

5.3.3 Recovery

Using the six (6) calibration standard solutions (5.1.3) and a sample solution spiked with from 100 µg to 500 µg, recovery of DEA should be not less than 90 %.

5.3.4 Calibration curve

Prepare a calibration curve by plotting the concentration of DEA (x-axis) versus peak area (y-axis) of quantitative ion (*m/z* 74) under selected ion monitoring mode (SIM) (see Figure 1), with the concentration of the sample solution in linear range with a correlation coefficient R^2 > 0,990. It is possible to dilute with ethanol when sample concentration falls outside the calibration range.

1) Agilent J&W DB-624 is a trademark of Agilent Technologies Inc. This information is given for the convenience of users of this document and does not constitute and endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

2) Rx® column is a trademark of Restek. This information is given for the convenience of users of this document and does not constitute and endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.4 Determination

The concentration of the DEA in the sample solution in micrograms per millilitre may then be calculated. The mass fraction *W*, in %, is obtained using Formula (1).

$$W = \frac{c \times V \times D_f}{m \times 10^6} \times 100 \quad (1)$$

where

W is the content of DEA (mass fraction), %;

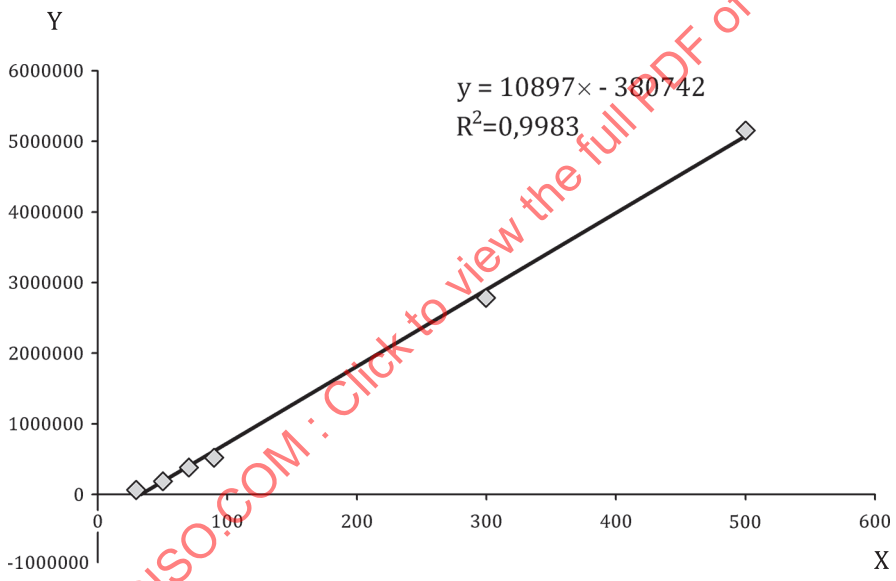
c is the concentration of DEA measured according to the standard working curve, µg/ml;

V is the final volume of the sample solution, ml;

m is the sample mass, g;

D_f is the dilution factor if any (if no step dilution used, $D_f = 1$).

Results are given with two decimals place.



Key

Y park area (quantitative ion: *m/z* 74)

X concentration (µg/ml)

Figure 1 — Calibration curve for DEA by quantitative ion (*m/z* 74) detection under SIM mode

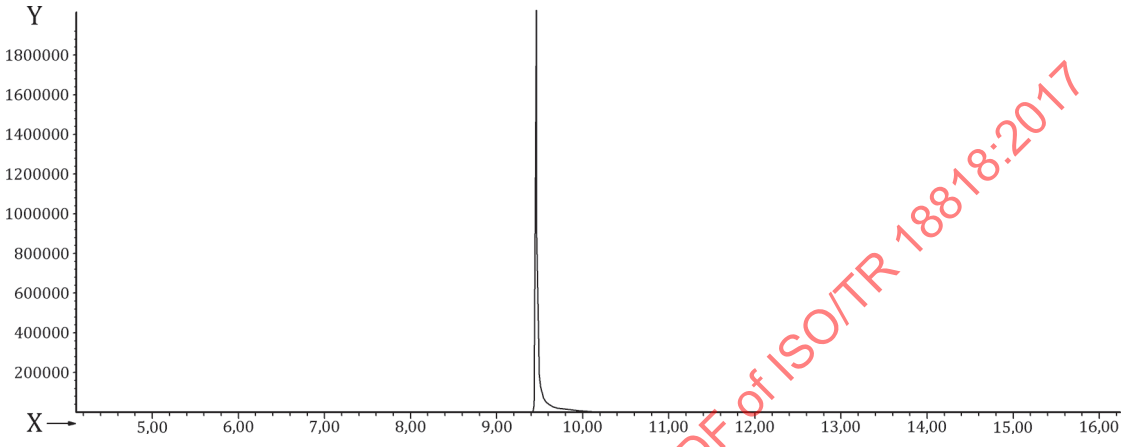
Annex A shows examples of the target ion (*m/z* 74) and the total ion chromatography of the DEA.

6 Limit of quantification

The limit of quantification (LoQ) of this method has been determined at 1 000 mg/kg (0,1 %). Observed detection limits may vary among different samples, depending upon the nature of interferences in the sample matrix and the characteristics of the specific instrumentation used.

Annex A
(informative)

Examples of typical GC-MS chromatogram of standard DEA



DEA (9,609 min)

Key

Y abundance

X time

Figure A.1 — Selected ion (m/z 74) scan chromatogram of DEA at 250 µg/ml (with DB-624 column)