



SLOVENSKI STANDARD
SIST EN 1811:1999

01-november-1999

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Reference test method for release of nickel from products intended to come into direct and prolonged contact with the skin

Referenzprüfverfahren zur Bestimmung der Nickellässigkeit von Produkten die in direkten und länger andauernden Kontakt mit der Haut kommen

Méthode d'essai de référence pour la libération du nickel par les produits qui sont destinés a venir en contact direct et prolongé avec la peau

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39.060 Nakit Jewellery

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EUROPEAN STANDARD
NORME EUROPÉENNE
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English version

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intended to come into direct and prolonged contact with the skin

Méthode d'essai de référence pour la libération du nickel
par les produits qui sont destinés à venir en contact direct
et prolongé avec la peau

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von Produkten die in direkten und länger andauernden
Kontakt mit der Haut kommen

This European Standard was approved by CEN on 10 October 1998.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 283 "Precious metals - Applications in jewellery and associated products", the secretariat of which is held by UNI.

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 May 1999, and conflicting national standards shall be withdrawn at the latest by May 1999.

Annex A, B, C, D and E are informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

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REPUBLIKA SLOVENSKO
ORGANIZACEK NA TECHNICKAS OUVAROVANIE
ORGANIZATION OF TECHNICAL STANDARDS OF SLOVAKIA
STANOVISKO

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MESTO BRATISLAVA



Introduction

Adverse skin reaction to nickel has been known for many decades. Nickel is now the most frequent cause of contact allergy in Europe, and 10% - 20% of the female population is allergic to nickel. Skin absorption of nickel ions, which are released from some nickel-containing materials in direct and prolonged contact with the skin, causes sensitisation. Further exposure to soluble nickel salts results in allergic contact dermatitis. It is known that sensitisation to nickel requires higher exposure levels than does the elicitation in already sensitised individuals. There is a large variation in the degree of sensitivity to nickel between individuals. This widespread health problem has forced the urgent introduction of a number of measures designed to reduce its prevalence. They include this standard which attempts to provide an *in-vitro* chemical test that correlates as far as possible with the variable human biological reactions that occur when metallic articles containing nickel are in direct and prolonged contact with the skin. The standard provides a measure of the amount of nickel release from an article immersed for one week in artificial sweat. It is a first attempt at the standardisation of a test method that previously has been used in research, and it is expected to require early revision in the light of further experience. The standard also describes the preparation of a reference material intended to assist a laboratory in achieving an acceptable precision.

Clinical patch-testing of a small selection of nickel-containing alloys and coatings on nickel-sensitized persons indicates that high and low results achieved with the present analytical method correspond closely with patch-test reactivity. Moreover, a nickel release rate threshold of 0,5 $\mu\text{g}/\text{cm}^2/\text{week}$ has been set in European Parliament and Council Directive 94/27/EC (OJ No. L188 of 22.7.94). In order to ensure that articles yielding values near this figure are not unnecessarily excluded from European trade as a result of the difficulties inherent in the test method, particularly when applied to intricately-shaped articles, the measured release figures are multiplied by a factor of 0,1. Materials recognized as causing sensitisation to nickel would not become acceptable by use of this adjustment. Application of this standard is confidently expected to reduce significantly the development of allergic contact dermatitis due to nickel. Experience of its use and further epidemiological and clinical research may justify changes to test procedure and/or interpretation of the test result.

1 Scope

This European Standard specifies a method for simulating the release of nickel from articles intended to come into direct and prolonged contact with the skin in order to determine whether such items release nickel at a rate greater than 0,5 $\mu\text{g}/\text{cm}^2/\text{week}$.

2 Principle

The item to be tested for nickel release is placed in an artificial sweat test solution for 1 week. The concentration of dissolved nickel in the solution is determined by atomic absorption spectrometry, inductively-coupled plasma spectrometry or other appropriate analytical method. The nickel release is expressed in micrograms per square centimetre per week ($\mu\text{g}/\text{cm}^2/\text{week}$).

3 Reagents

Except where indicated, all reagents shall be of recognized pro analysis, p.a., grade or better and shall be free of nickel.

3.1 Deionized and aerated water

Fill a tall-form 2-l beaker with deionized water, specific conductivity max 1 $\mu\text{S}/\text{cm}$. Saturate with air by attaching a gas distribution tube (porosity 1) to a cork and positioning the lower end of the tube on the bottom of the beaker. Allow grease-free air to flow at a rate of 150 ml/min for 30 min.

3.2 Sodium chloride**3.3 DL-Lactic acid, $\rho = 1,21 \text{ g/ml}$, $>88 \%$ (m/m)****3.4 Urea****3.5 Ammonia solution, $\rho = 0,91 \text{ g/ml}$, 25% (m/m)****3.6 Dilute ammonia solution, 1% (m/m)**

Transfer 10 ml of ammonia solution (3.5) into a 250-ml beaker containing 100 ml of deionized water. Stir and cool to room temperature. Transfer the solution to a 250-ml volumetric flask and make up to volume with deionized water.

3.7 Nitric acid, $\rho = 1,40 \text{ g/ml}$, 65% (m/m)**3.8 Dilute nitric acid, approximately 5% (m/m)**

Transfer 30 ml of nitric acid (3.7) into a 500-ml beaker containing 350 ml of deionized water. Stir and cool to room temperature. Transfer the solution to a 500-ml volumetric flask and make up to volume with deionized water.

3.9 Degreasing solution

Dissolve 5 g of an anionic surface-active agent such as sodium dodecylbenzene sulfonate or sodium alkylaryl sulfonate in 1000 ml water. An appropriately diluted, neutral, commercially-available detergent may be used.

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3.10 Wax or lacquer (suitable for electroplating purposes) capable of protecting a surface from nickel release.

The wax or lacquer shall be shown to prevent nickel release from a nickel-releasing surface when one or more coats of the wax or lacquer are applied in the same manner as on a test sample, and tested for nickel release according to clause 6 (see annex C).

4 Apparatus**4.1 A pH-meter, accurate to $\pm 0,02 \text{ pH}$**

4.2 An analytical spectrometer capable of detecting a concentration of 0,01 mg nickel per litre. The instrument shall, after optimization, meet the performance criteria given in 4.2.1 and 4.2.2.

It is recommended that either an inductively-coupled plasma - optical emission spectrometer or an electrothermal excitation atomic absorption spectrometer is used.

4.2.1 Minimum precision

The standard deviation of 10 measurements of the absorption of a full matrix calibration solution containing 0,05 mg nickel per litre shall not exceed 10 %.

4.2.2 Limit of detection

The limit of detection shall be considered as twice the standard deviation of 10 measurements of the absorbance of a full matrix solution containing nickel at a concentration level selected to give an

absorbance just above that of the zero calibration solution. The limit of detection of nickel in a matrix similar to the final test solution shall be better than 0,01 mg/l.

4.3 Thermostatically controlled water-bath or oven, capable of maintaining a temperature of (30 ± 2) °C.

4.4 A vessel with lid, both composed of a non-metallic, nickel-free and nitric-acid-resistant material, such as glass and/or polypropylene and/or polytetrafluoroethylene and/or polystyrene. The sample shall be suspended in the liquid by a holder made from the same materials as listed above, so as to minimize contact of the sample area (5.1.1) with the walls and base of the vessel. The size and shape of vessel and holder shall be chosen so as to minimize the volume of test solution required to completely cover the object to be tested.

In order to remove any trace of nickel, the vessel and holder shall be pre-treated by being stored in a solution of dilute nitric acid (3.8) for at least 4 h. After acid treatment, rinse the vessel and holder with deionized water and dry.

5 Samples

5.1 Sample area

5.1.1 Definition of sample area

Only the surface(s) of an item that comes into direct and prolonged contact with the skin shall be analyzed. In this standard such surfaces are defined as "sample area".

5.1.2 Determination of sample area

Determination of the sample area (a) in square centimetres is achieved by marking the contour of the sample area assuming that the item is worn or used as intended (see annex C). In order to achieve the required degree of analytical sensitivity, a minimum sample area of 0,2 cm² shall be tested. If necessary, identical items may be treated together to obtain this minimum area.

NOTE: If an item is being tested to ascertain its conformity with Directive 94/27/EC, the accuracy with which the sample area of the item has to be determined is dependent on the nickel release of this item. The closer the nickel release is to 0,5 µg/cm²/week, the limit laid down in the directive, the more accurately the surface area has to be determined.

5.1.3 Areas other than sample areas

In order to prevent release of nickel from areas other than the sample area, such areas shall be removed or protected from the test solution. This may be achieved after degreasing (see 5.2) by, for example, the application of one or more coatings of a wax or lacquer which has been shown to protect from nickel release (3.10). Annex C gives guidance on the coating of protected areas prior to testing. Where it is not feasible to remove or protect all areas other than the sample area, for example with certain watch bracelets, such unprotected surfaces shall be considered as part of the sample area.

NOTE: If, when non-significant surfaces are considered to be part of the sample area, the nickel release from the item is found to be unacceptable, consideration should be given to dismantling the item and testing any internal components for nickel release. If the nickel release from such internal components is significant it might be appropriate to test the external components on their own, assuming that they are available, or the materials from which the item has been manufactured (see annex D).

5.2 Sample preparation

Gently swirl the sample for 2 min in degreasing solution (3.9) at room temperature. Rinse thoroughly with deionized water and dry. After degreasing, items should be handled with plastic forceps or clean protective gloves.

NOTE: This cleaning stage is intended to remove extraneous grease and skin secretions due to handling, but not any protective coatings. However, it will also substantially remove any nickel contamination that might be present on the surface of the item. If there is a requirement to determine this nickel the cleaning stage should be omitted. However, it should be appreciated that omission of this cleaning stage might itself affect the nickel release from the item.

5.3 Reference disc

As a quality control check, the nickel release from a reference disc may be determined (see annex A and annex B).

If used, it is important that both sides of a reference disc are abraded before each test. A minimum of 0,05 mm shall be abraded from each surface using wet emery paper No. 600 followed by No. 1200. The disc is then degreased in the same way as the sample (5.2).

6 Procedure

6.1 Preparation of test solution

The test solution representing artificial sweat consists of deionized and aerated water (3.1) containing:

- 0,5 % (*m/m*) sodium chloride (3.2);
- 0,1 % (*m/m*) lactic acid (3.3);
- 0,1 % (*m/m*) urea (3.4); and
- ammonia solution, 1 % (3.6).

Transfer (1,00 ± 0,01) g of urea, (5,00 ± 0,01) g of sodium chloride and (940 ± 20) µl of lactic acid to a 1000-ml beaker. Add 900 ml of freshly prepared deionized and aerated water (3.1) and stir until all the added reagents are completely dissolved. Calibrate the pH-meter in accordance with the manufacturer's instructions using freshly prepared buffer solutions. Immerse the pH electrode into the test solution. Stir gently and carefully add dilute ammonia solution (3.6) until a stable value of (6,50 ± 0,10) pH is reached. Transfer the solution to a 1000-ml volumetric flask and make up to volume with deionized and aerated water. Before use, ensure that the pH of the test solution is in the range 6,40 to 6,60. Use the test solution within 3 h of preparation.

6.2. Release procedure

6.2.1 Place the sample, suspended by its holder, in the test vessel (4.4). Add an amount of test solution corresponding to approximately 1 ml per cm² sample area. The suspended sample shall be totally immersed. However, it is not essential to immerse areas which are completely protected by wax or lacquer. The minimum volume of test solution added shall be 0,5 ml irrespective of the surface area. Note the sample area and the amount of the test solution used. Close the vessel with a tight lid in order to prevent evaporation of the test solution. Leave the vessel undisturbed in a thermostatically-controlled water-bath or oven (4.3) at (30 ± 2) °C for 168 h without agitation.

If a reference disc (5.3) is to be determined, it should be suspended in 3 ml of test solution and treated in the same manner as a sample.

6.2.2 After 1 week, remove the sample from the test solution and rinse it with a small quantity of deionized water, adding the rinsings to the test solution. Quantitatively transfer the test solution to an appropriately-sized (see note) volumetric flask washed with acid. In order to prevent redeposition of dissolved nickel, add dilute nitric acid (3.8) and deionized water to the test solution to achieve a

concentration of about 1 % nitric acid when the flask is made up to volume (V ml). The minimum final volume to which the test solution may be diluted is 2 ml.

NOTE: The choice of volumetric flask size should take into account the sensitivity of the instrumentation used for the nickel determination (see 4.2).

6.3 Determination of nickel

Determine the nickel content of the test solution using an analytical spectrometer (see 4.2)

6.4 Number of replicates

Whenever possible, the determination shall be carried out on at least two identical samples.

6.5 Blank tests

Duplicate blank tests shall be carried out at the same time as the testing of the sample. Identical vessels and holders shall be used and the test procedure is identical except that no sample is placed in the vessels. Identical amounts of test solution, rinsing water and dilute nitric acid shall be used.

7 Calculations

7.1 Nickel release

The nickel release of a sample, d , expressed in micrograms per square centimetre per week ($\mu\text{g}/\text{cm}^2/\text{week}$), is given by the equation:

$$d = \frac{V \times (C_1 - C_2)}{1000 \times a}$$

where:

a is the sample area of the test object, in square centimetres (cm^2);

V is the dilution volume of the test solution, in millilitres (ml);

C_1 is the nickel concentration in the diluted test solution after 1 week, in micrograms per litre ($\mu\text{g}/\text{l}$);

C_2 is the mean value of the nickel concentration in the blank solutions after 1 week, in micrograms per litre ($\mu\text{g}/\text{l}$).

7.2 Interpretation of results

Multiply the result, d , established in 7.1 by 0,1 to obtain an adjusted analytical figure.

A sample shall be deemed to have a nickel release of more than $0,5 \mu\text{g}/\text{cm}^2/\text{week}$ if the adjusted figure is greater than $0,5 \mu\text{g}/\text{cm}^2/\text{week}$.

NOTE: Due to the imprecision of the method specified in this standard, a multiplication factor is required to adjust the analytical result to take into consideration the factors detailed in annex A, including the performance characteristics obtained from an interlaboratory trial.