Screening tests for nickel release from alloys and coatings in items that come into direct and prolonged contact with the skin
National foreword

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Summary of pages

This document comprises a front cover, an inside front cover, the CR title page, pages 2 to 10, an inside back cover and a back cover.

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Screening tests for nickel release from alloys and coatings in items that come into direct and prolonged contact with the skin

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Foreword

This document (CR 12471:2002) 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.
Introduction

This document has been developed as a simple, quick and inexpensive means for qualitatively testing for nickel release from (mainly) consumer items. It has particular relevance in relation to allergic contact dermatitis due to nickel allergy. The tests described are quick and easy to conduct and two of them are suitable for application outside of the laboratory.

European Parliament and Council Directive 94/27/EC (OJ No. L 188 of 22.7.94) has set a nickel release rate threshold of 0.5 µg/cm²/week. Although the present document will give information concerning nickel release, results obtained from its application do not constitute confirmation or otherwise of compliance with the directive. In order to show compliance with the directive, it is necessary that items are tested in accordance with European Standards EN 1810, EN 1811 or EN 12472, as appropriate, depending upon the nature of the item to be tested.
1 Scope

This document presents a screening procedure, based primarily on the use of dimethylglyoxime, for the detection of nickel release from items that come into direct and prolonged contact with the skin.

The tests provide qualitative, not quantitative, results.

NOTE - EN 1811 specifies a quantitative reference test for the release of nickel.

2 Short description of the methods

The test methods are based on the formation of a coloured complex when nickel ions come into contact with dimethylglyoxime or dithiooxamide. In order to increase the sensitivity of the method, pre-treatment with artificial sweat and heat is used to induce corrosion of the surface, simulating the influence of sweat when the item is in contact with the skin. This screening method gives a result in a short time. The result is indicative and provides guidance when evaluating items for nickel release.

3 Reagents

All reagents shall be of pro analysi grade or better.

3.1 Deionized water

3.2 Ammonia solution, about 10 % (m/m) NH₃

NOTE - This solution may be prepared from a more concentrated ammonia solution; for example, one containing 24 % or 30 % (m/m) NH₃.

3.3 Sodium chloride, NaCl

3.4 Lactic acid, CH₃CHOHCOOH, ρ = 1.21 g/ml, > 88 %

3.5 Urea, CO(NH₂)₂

3.6 Dimethylglyoxime, C₄H₈N₂O₂, 99 %, or test strips for the detection of nickel, containing dimethylglyoxime or other colorimetric reagent(s) with approximately equivalent selectivity and sensitivity to nickel.

3.7 Ethanol, C₂H₅OH, > 95 %

3.8 Hydrogen peroxide, H₂O₂, approximately 30 % (m/V) solution (100 volume). (Not required for the pre-test, 5.3.4 or the field test, 5.3.6)

3.9 Dithiooxamide (rubeanic acid), C₂H₄N₂S₂. (Not required for the pre-test or the field test)

3.10 Sodium acetate trihydrate, C₂H₃NaO₂3H₂O. (Not required for the pre-test or the field test)

3.11 Acetic acid, glacial, C₂H₄O₂. (Not required for the pre-test or the field test)

4 Equipment

4.1 Flat-bottomed dish, made of glass or other non-metallic material. (Not required for the pre-test)

4.2 Thermometer, (0°C - 100°C) ± 1°C
4.3 Pasteur pipette or, for the field test, a drop-dispensing bottle capable of dispensing drops with an approximate volume of 50 µl.

4.4 Cotton-wool-tipped sticks (white)

4.5 pH meter or narrow-range pH paper

4.6 Laboratory oven, capable of maintaining a temperature of 50°C ± 3°C (required for the laboratory test, 5.3.5)

4.7 Heating/drying apparatus (required only for the field test)

4.7.1 Hand-held hair dryer, or

4.7.2 Apparatus consisting of a light bulb, reflector type, (IEC 887: R80; 60 W to 100 W) mounted vertically downwards in a lamp holder positioned above a flat base, such that the distance of the face of the bulb above the flat base may be varied between approximately 40 mm and 120 mm.

5 Procedure

5.1 Preparation of solutions

Unless otherwise specified, the following solutions are stable for 6 months at temperatures below 25°C.

5.1.1 Dimethylglyoxime, 0.8% (m/V) alcoholic solution. Weigh 0.8 g ± 0.05 g of dimethylglyoxime (3.6), dissolve and make up to 100 ml in ethanol (3.7).

5.1.2 Artificial sweat. Transfer 1 g ± 0.02 g urea (3.5), 5 g ± 0.1 g sodium chloride (3.3) and 1.13 g ± 0.02 g (940 µl ± 20 µl) lactic acid (3.4) into a 2-litre beaker. Add 1000 ml deionized water (3.1) and stir. Using a pH meter or pH paper (4.5), adjust the pH to 6.5 ± 0.2 by the dropwise addition of ammonia solution (3.2) with stirring. Artificial sweat is stable for 6 months when kept in the dark below 8°C in a closed container.

NOTE - The use of a pH meter is preferable to the use of narrow-range pH paper.

5.1.3 Dithiooxamide, 0.5% (m/V) alcoholic solution. Weigh 0.5 g ± 0.05 g of dithiooxamide (3.9), dissolve and make up to 100 ml in ethanol (3.7).

5.1.4 Sodium acetate buffer solution, pH 4.5. Weigh 5.6 g sodium acetate trihydrate (3.10) and add 2.4 ml glacial acetic acid (3.11). Dissolve and make up to 10 ml with water.

5.2 Sample preparation

5.2.1 The surfaces to be tested are those that come into direct and prolonged contact with the skin. The surface(s) of the item to be tested shall be cleaned with ethanol (3.7) using a cotton-wool-tipped stick (4.4).

NOTE 1 - 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 salts present on the surface of the test item. If there is a requirement to detect the presence of surface contamination by nickel, this cleaning stage should be omitted.

NOTE 2 - An item may be composed of parts made of different materials, each of which may require testing if they come into direct and prolonged contact with the skin.

NOTE 3 - Contamination by objects containing nickel (paper-clips, rivets, coins, etc.) may give false positive results if such objects come into contact with test items, surfaces, reagents or the hands. This possibility should be eliminated by avoidance of nickel-containing objects, washing the hands before performing the tests and performing blank tests.
5.2.2 The presence of coatings, such as paint, lacquer and electroplate, can prevent the detection of a nickel-releasing substrate. Therefore, abrasion of the surface prior to testing for nickel-release should be considered, especially if a negative result (see 6.2) has been obtained on the unabraded item. This may be achieved using emery paper, emery board or other nickel-free abrasive material.

CAUTION This procedure is likely to damage the item.

NOTE - If a positive result is obtained in these circumstances, testing in accordance with EN 12472 is required to check compliance with EU Directive 94/27/EC.

5.3 Test methods

5.3.1 The person carrying out the tests shall have a normal colour vision in regard to being able to detect red and pink colours.

5.3.2 Check the reactivity of the test solutions, as necessary, by applying the test to a known nickel-releasing surface, e.g. a cupro-nickel coin.

5.3.3 Either conduct the pre-test (5.3.4) and/or the laboratory test (5.3.5) or the field test (5.3.6).

a) If the pre-test is conducted and a positive result (red colouration) is observed, further testing is unnecessary unless the presence of iron is suspected (see 5.3.8);

b) If the pre-test is conducted and a negative result (absence of red colouration) is observed, conduct the laboratory test (5.3.5) or the field test (5.3.6).

NOTE - The pre-test only gives a positive result in the presence of nickel salts or where nickel is available for release from an item without prior corrosion (see clause 2).

5.3.4 Pre-test for nickel release: moisten a cotton-wool-tipped stick (4.4) with one or two drops of dimethylglyoxime solution (5.1.1) and one drop of ammonia solution (3.2). Check that there is no discolouration. Rub firmly the cotton wool tip for 15 s against the surface to be tested. View the stick against a white background. The appearance of a red colour, from light pink to strong cerise, indicates nickel release.

5.3.5 Laboratory test: place the test item on a dish (4.1) and pre-heat it to approximately 50°C. Using a Pasteur pipette, transfer one drop of artificial sweat (5.1.2) onto the surface to be tested. Dry the item in the laboratory oven (4.6) until its surface is completely dry. The temperature shall be 50°C ± 3°C. Drying time will be about 15 min. Perform the test for nickel release (5.3.7, 5.3.8 or 5.3.9, as appropriate).

5.3.6 Field test: place the test item on a dish (4.1) and using a Pasteur pipette or a drop-dispensing bottle (4.3) put one drop of artificial sweat (5.1.2) on the surface to be tested. Dry the surface completely with the hair dryer (4.7.1). If necessary, keep the item in place using any suitable means. Place a thermometer (4.2) close to the test item. The temperature shall not exceed 50°C.

Alternatively, the test item can be dried by the heat from an electric light bulb using the equipment described in 4.7.2. The light bulb is switched on and allowed to warm up. Raise or lower the lamp holder to obtain a constant temperature of approximately 50°C just above the surface on the flat base directly beneath the lamp. Place the test item on a dish directly beneath the centre of the lamp. Pre-heat the item for about 10 min then put one drop of artificial sweat on the surface to be tested. Allow the surface to dry completely.

Perform the test for nickel release (5.3.7).
5.3.7 Testing for nickel release: allow the item to cool for approximately 5 min. Moisten a cotton-wool-tipped stick (4.4) with one or two drops of dimethylglyoxime solution (5.1.1) and one drop of ammonia solution (3.2). Check that there is no discolouration. Place the tip of the cotton-wool-tipped stick onto the area to be tested and rub gently for 5 s. View the stick against a white background. The appearance of a red colour, from light pink to strong cerise, indicates nickel release.

Using test strips for the detection of nickel: Allow the item to cool and immediately put one drop of ammonia solution (3.2) on the dried salts. Place the test strip (3.6) onto the treated area for 5 s. View the strip against a white background. The appearance of a red colour, from light pink to strong cerise, indicates nickel release.

Note - Due to the corrosion induced by the artificial sweat and formation of salts on the surface, shorter time and pressure is needed for the testing in 5.3.7 than when performing the pre-test (5.3.4).

5.3.8 Checking for interference by iron (laboratory test only): when stainless steel or other iron-containing items are tested, ferrous ions can cause a red or reddish-brown colouration. This colouration can interfere with the detection of nickel. In order to eliminate the influence of iron, the test (5.3.7) should be modified in the following way. After allowing the test item to cool for approximately 5 min, moisten the tip of a cotton-wool-tipped stick (4.4) with one or two drops of dimethylglyoxime solution (5.1.1) and one drop of ammonia solution (3.2). Place a drop of hydrogen peroxide solution (3.8) onto the surface to be tested. This oxidises ferrous ions (Fe$^{2+}$) to ferric ions (Fe$^{3+}$). Rub the test area gently with the cotton wool tip for 5 s. View the stick against a white background. The appearance of a reddish colour indicates nickel release. The appearance of other colours can mask a pale pink colour and hence conceal the presence of nickel.

**WARNING** 100 volume hydrogen peroxide solution is corrosive and can cause burns. In contact with combustible material it can cause fire.

If test strips are used, oxidation may be achieved by leaving the strip in the air for 15 min, rather than by the addition of hydrogen peroxide solution to the surface to be tested.

**NOTE** - Some test strips contain masking agents for iron. For more information read the manufacturers’ instructions.

5.3.9 Confirmation of nickel release: if desired, the release of nickel from an item may be confirmed after repeating the sample preparation (5.2) and the laboratory test (5.3.5). It shall not be performed directly after 5.3.7, testing for nickel release.

Allow the object to cool for approximately 5 min. Place the tip of a cotton-wool-tipped stick moistened with one drop of acetate buffer (5.1.4) and one or two drops of dithiooxamide solution (5.1.3) onto the surface to be tested and rub gently for 5 s. View the stick against a white background. The appearance of a black-violet colour indicates nickel release.

**NOTE** - This test is not intended as a substitute for testing with dimethylglyoxime (see 5.3.7), and it is recommended primarily for the confirmation of nickel release. However, because of its ability to discriminate between nickel and iron release, it may be performed in addition to 5.3.7 and/or 5.3.8 when testing items that contain iron, e.g. stainless steels, and used to assist in the interpretation of results.

6 Interpretation of results

6.1 Positive result

Formation of a red colour, from light pink to strong cerise, with dimethylglyoxime indicates that the nickel release from a tested surface is likely to be greater than 0.5 µg/cm²/week, and a positive result should be reported. Formation of a black-violet colour with dithiooxamide confirms a positive result obtained with dimethylglyoxime.
6.2 Negative result

No colour change in both or either of these tests, indicates an absence of nickel release, and a negative result should be reported. However, such a result should be interpreted cautiously since these tests are of short duration and the test conditions are not comparable with those in EN 1811. The apparent absence of nickel release should be confirmed by EN 1811 or EN 12472 (followed by EN 1811), as appropriate.

6.3 Uncertain result

Apart from nickel, colouration in these tests can occur from metals such as cobalt, copper and palladium and mask any red colouration from nickel. Where colours other than red are obtained, the result should be reported as uncertain. In such cases, it is advisable to apply the appropriate reference method, EN 1811 or EN 12472 (followed by EN 1811).

7 Test report

The test report shall include at least:

a) Identification of the sample including source, date of receipt, form of sample;

b) A reference to this document and to the test(s) performed;

c) Nickel release described in accordance with clause 6 (i.e. positive, negative or uncertain), specifying which part(s) of the item has(have) been tested;

d) Details of any deviations from the test procedures;

e) Any unusual features observed during the testing;

f) Date of test;

g) Signature of the operator.
Bibliography


[2] EN 1811:1998  Reference test method for release of nickel from products intended to come into direct and prolonged contact with the skin


NOTE The above standards were notified as European harmonised standards in the Official Journal of the European Communities (OJ) No. C 205, 20.7.1999, p. 5