TECHNICAL SPECIFICATION

**ISO/TS 24348**

Third edition
2014-02-01

# Ophthalmic optics — Spectacle frames — Method for the simulation of wear and detection of nickel release from metal and combination spectacle frames

*Optique ophtalmique — Montures de lunettes — Méthode de simulation de l'usure et de détection de la libération du nickel de montures de lunettes en métal et combinées*

Reference number
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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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# Foreword

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The committee responsible for this document is ISO/TC 172, *Optics and photonics*, Subcommittee SC 7, *Ophthalmic optics and instruments*.

This third edition cancels and replaces the second edition (ISO/TS 24348:2007), which has been technically revised.

# Introduction

Adverse skin reaction to nickel has been known for many decades. Nickel is now the most frequent cause of contact allergy, and a significant proportion 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 sensitization. Further exposure to soluble nickel salts results in allergic contact dermatitis. It is known that sensitization to nickel requires higher exposure levels than does the elicitation in already sensitized individuals. There is a large variation in the degree of sensitivity to nickel between individuals.

This widespread health problem has forced the introduction of a number of measures designed to reduce its prevalence. They include this Technical Specification which provides two procedures for testing those parts of metal and combination spectacle frames that come into direct and prolonged contact with the skin.

Clause 4 specifies a method for accelerated wear to simulate two years' use of coated metal and combination spectacle frames. The coatings might include rolled gold covering, electro- and other plating methods, varnish and other organic treatments. Clause 5 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. It provides a measure of the amount of nickel release from a spectacle frame when immersed for one week in artificial sweat.

Clinical patch-testing of a selection of nickel-containing alloys and coatings on nickel-sensitized persons indicates that high and low results achieved with the analytical method in this Technical Specification correspond closely with patch-test reactivity. Moreover, a nickel release rate threshold of 0,5 µg/cm$^2$/week was set in the European Parliament and Council, originally in Directive 94/27/EC (OJ No. L188 of 1994-07-22) and transferred to Regulation (EC) 1907/2006 (OJ No. L396/1 of 2006-12-30, REACH). [6] 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 sensitization to nickel would not become acceptable by use of this adjustment. Application of this Technical Specification is confidently expected to significantly reduce the development of allergic contact dermatitis due to nickel.

NOTE Experience of its use and further epidemiological and clinical research can justify changes to test procedure and/or interpretation of the test result

# Ophthalmic optics — Spectacle frames — Method for the simulation of wear and detection of nickel release from metal and combination spectacle frames

## 1 Scope

This Technical Specification specifies methods for accelerated wear and corrosion, to be used prior to the detection of nickel release from coated metal and combination spectacle frames, and for detecting the release of nickel from those parts of metal and combination spectacle frames, whether coated or not, intended to come into direct and prolonged contact with the skin, in order to determine whether such parts release nickel at a rate greater than 0,5 µg/cm$^2$/week.

This Technical Specification aims to control those spectacle frames which, if produced with materials and/or surface treatments containing nickel, can be worn by nickel-sensitized persons.

## 2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable to its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 12870, *Ophthalmic optics — Spectacle frames — Requirements and test methods*

## 3 Requirement

Those parts of metal and combination spectacle frames that come into direct and prolonged contact with the skin of the wearer shall not have a nickel release greater than 0,5 µg/cm$^2$/week when tested according to this Technical Specification.

Spectacle frames having a non-nickel coating shall be subjected to the corrosion and wear pretreatment in Clause 4 which simulate two years' typical wear.

For spectacle frames that are made of homogeneous alloy or pure metal and are uncoated, go directly to the nickel release test procedure in Clause 5.

See also Annex D.

The parts to be tested shall include:

— the rear surface of rims;

— the rear and lower surface of the bridge, the rear and upper surface of any brace bar and any other nasal-bearing surfaces, including metal nose pads;

— sides, excluding the joints and the zone immediately around the joints, and parts intended to be protected by plastic endcovers (tips).

# 4 Method for the corrosion and abrasion of coated metal spectacle frames before the determination of nickel release

## 4.1 Principle

The items to be tested are exposed to a corrosive atmosphere before being placed in a tumbling barrel together with a wear medium of abrasive paste and granules. The barrel is rotated so as to subject the test pieces to wear from the wear medium. The items are then tested for nickel release in accordance with Clause 5.

## 4.2 Reagents and materials

### 4.2.1 General

Except where indicated, all reagents and materials that can come into contact with samples or reagents shall be demonstrably free of nickel, and all reagents shall be of recognized analytical grade or better.

### 4.2.2 Reagents and materials for the corrosion procedure

**4.2.2.1 Container**, with a lid and a device for suspending the test pieces, and all parts made of inert material (e.g. glass or plastic).

**4.2.2.2 Corrosive medium**, prepared by dissolving 50 g DL-lactic acid, >85 % purity, and 100 g sodium chloride in 1 000 ml deionized water.

**4.2.2.3 Degreasing solution**, being an appropriately diluted, neutral, commercially available detergent, e.g. a 0,5 % aqueous solution of sodium dodecylbenzene sulfonate.

**4.2.2.4 Deionized water**, specific conductivity maximum 1 µS/cm.

**4.2.2.5 Laboratory oven**, capable of maintaining a temperature of (50 ± 2) °C.

### 4.2.3 Reagents and materials for the wear procedure

**4.2.3.1 Tumbling barrel and retaining assembly**, in accordance with the following description:

— barrel of hexagonal cross-section and internal diameter of 19 cm perpendicular distance between opposite sides designed to rotate around its axis, which is orientated horizontally (see Figure 1);

— retaining assembly, suitable for attaching the test items so that they do not come into contact with each other during tumbling;

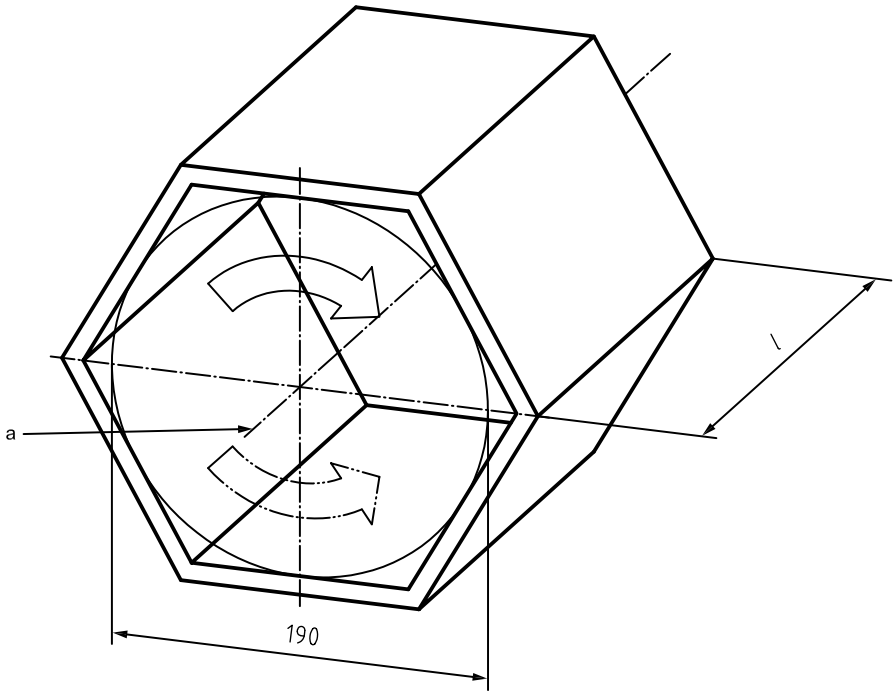
— retaining assembly, with items attached, to be inserted into the barrel for tumbling.

NOTE Information on sourcing suitable equipment is available from the ISO Central Secretariat.

**4.2.3.2 Rotating system**, capable of imparting to the barrel (4.2.3.1) a constant (30 ± 2) rotations per minute. The rotating system shall be capable of allowing the direction of rotation to be reversed.

NOTE Information on sourcing suitable equipment is available from the ISO Central Secretariat.

Dimensions in millimetres




**Key**

*l* length of barrel, as required

a Axis of rotation.

**Figure 1 — View of tumbling barrel**

**4.2.3.3 Abrasive paste**, produced for dry-tumbling barrels and comprising:

— 6 % to 8 % ester wax of montanic acids – Wax E [CAS No. 73138-45-1];

— 3 % octadecanoic acid (stearic acid) [CAS No. 57-11-4];

— 30 % to 35 % petroleum distillates, hydrotreated light paraffinic [CAS No. 64742-55-8];

— 2 % polyethylene glycol cetyl/oleyl ether [CAS No. 68920-66-1] or triethanolamine [CAS No. 102-71-6];

— 48 % silicon dioxide (quartz) 200 µm mesh size [CAS No. 14808-60-7];

— 6 % to 9 % deionized water.

NOTE Information on sourcing a suitable paste is available from the ISO Central Secretariat.

**4.2.3.4 Granules**, composed of outer shells of coconuts, walnuts, peanuts and almonds, mixed in a ratio 1:1:1:1 by weight, ground and sieved to give a mixture of particles having dimensions of between 0,8 mm and 1,3 mm.

NOTE Information on sourcing suitable granules is available from the ISO Central Secretariat.

**4.2.3.5 Wear medium**, composed of abrasive paste (4.2.3.3) and wear granules (4.2.3.4) which are mixed as indicated in 4.5.1. Before use, the required amount of granulate shall be conditioned in standard laboratory conditions for at least 24 h.

**4.2.3.6 Retaining assembly**, consisting of a threaded rod which carries three metal hexagonal plates (see Figures 2 and 3). The end plate, A, is drilled part way through with holes of nominal diameter 1,5 mm, or as appropriate, positioned 10 mm to 15 mm from the edge of the plate, to take the ends of the tips of the sides. The next plate, B, is perforated with holes of nominal diameter 5,0 mm, or as appropriate, positioned 10 mm to 15 mm from the edge of the plate, to take the joint ends of the sides, together with an aperture of 40 mm nominal diameter to act as a filling hole for the abrasive mixture. A silicone rubber sheet with small holes matching the position of those in plate B holds the sides to prevent them from rotating in the assembly. The final plate, C, is undrilled apart from the hole for the threaded rod. A threaded nut on the inside of the last two plates holds them the required distance from plate A, while a second nut on the outside clamps the assembly together. The volume between plates A and B is approximately 5 l ± 0,5 l, but will vary depending upon the length of the sides or width of the spectacle fronts to be tested.

Dimensions in millimetres

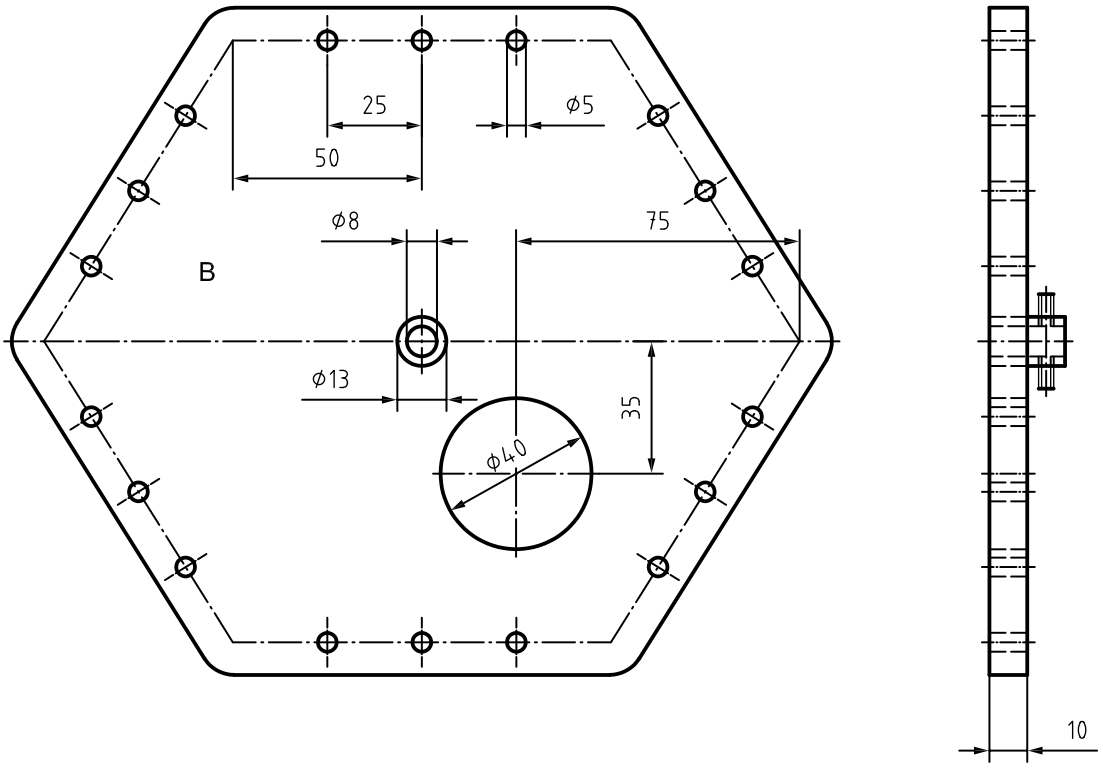
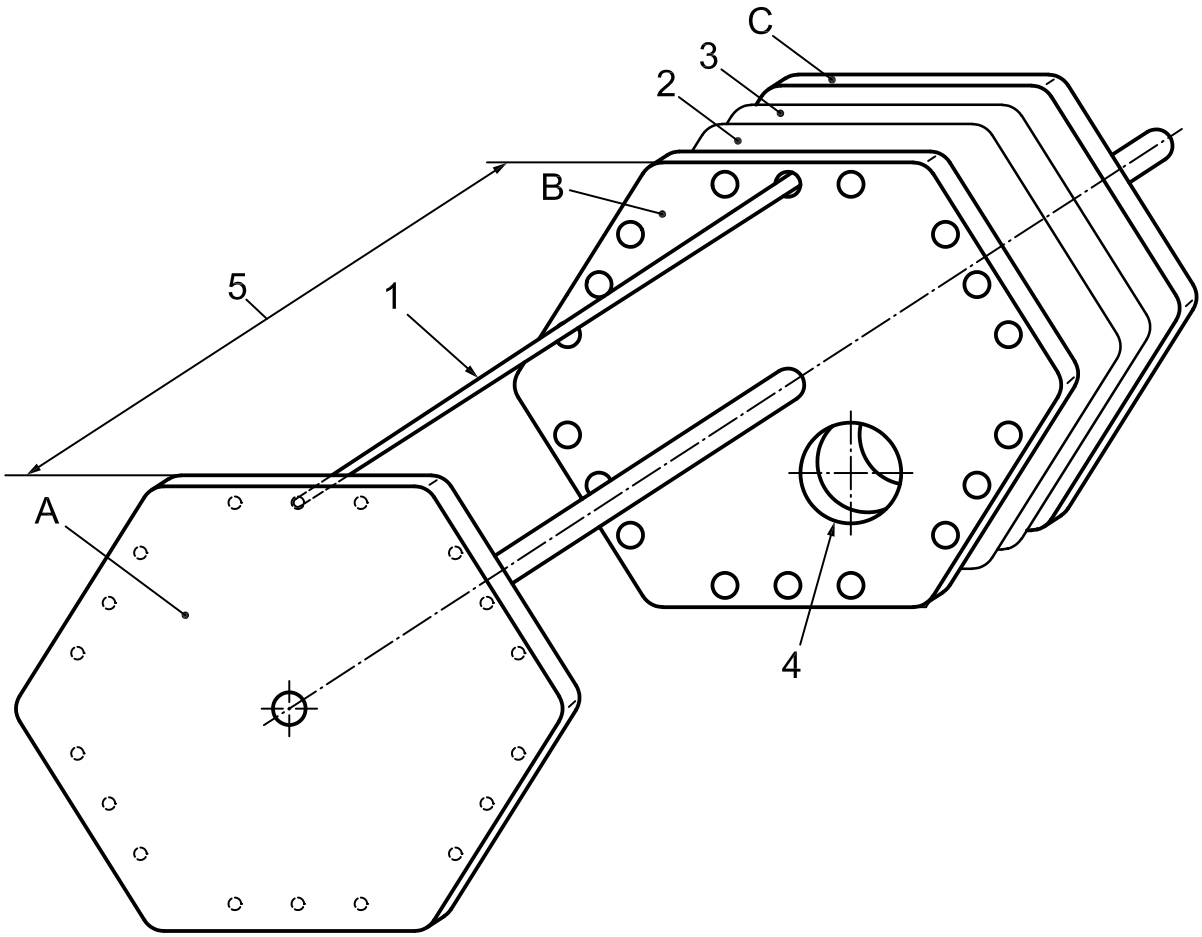



**Figure 2 — Plan view of the upper part of the tumbling barrel — Component B**




**Key**

| | | | |
|---|---|---|---|
| 1 | sample side | 4 | fill hole |
| 2 | silicone sheet, perforated | 5 | adjust as required |
| 3 | silicone sheet, plain | | |

**Figure 3 — Exploded diagram of retaining assembly for spectacle sides**

## 4.3 Sample preparation

Before being subjected to the corrosion procedure (see 4.4) and the wear procedure (see 4.5), spectacle sides and fronts shall be separated from each other, and endcovers (side tips) removed from sides and nose pads from fronts where appropriate. If the spectacle frame is to be subject to the accelerated wear procedure given in this Technical Specification, then it shall be fitted with test lenses as specified in ISO 12870 before being subjected to the accelerated wear procedure.

NOTE 1 Parts of items which are not intended to come into prolonged contact with the skin can be removed before being subjected to corrosion and/or wear.

Gently swirl the sample(s) for 2 min in degreasing solution (4.2.2.3) at room temperature. Rinse thoroughly with deionized water (4.2.2.4) and gently dry with absorbent paper. After degreasing, samples should be handled with plastic forceps or clean protective gloves.

NOTE 2 This cleaning stage is intended to remove extraneous grease and skin secretions due to handling, but not any protective coatings.

## 4.4 Corrosion procedure

Suspend the items to be tested a few centimetres above the corrosive medium (4.2.2.2) in a closed container (4.2.2.1) placed in the laboratory oven (4.2.2.5) for 2 h at 50 °C. Remove the container from the oven and carefully open it under a fume hood. Rinse the items with deionized water (4.2.2.4). Place on absorbent paper and allow to dry at room temperature for about 1 h, then perform the wear procedure specified in 4.5 without delay.

NOTE This stage is intended to affect metallic coatings as well as lacquers and plastic coatings.

## 4.5 Wear procedure

### 4.5.1 Preparation of wear medium

Weigh a sufficient quantity of wear granules (4.2.3.4) in order to fill the tumbling barrel (4.2.3.1) to half its depth. Add 7,5 g of abrasive paste (4.2.3.3) for every kilogram of wear granules and homogenize by rotating in the barrel for 5 h. If the wear medium has not been used within 1 week, re-homogenize by rotating it in the barrel for 1 h.

NOTE This procedure coats the granules with the abrasive paste, forming the wear medium that is used to simulate wear.

Keep the wear medium in a closed container until use and between uses.

After two wear procedures, add 7,5 g more abrasive paste for every kilogram of wear medium. Re-homogenize the wear medium by rotating it in the barrel for a further 5 h.

After a total of four wear procedures, discard the wear medium and prepare fresh material.

### 4.5.2 Attachment of test items

Attach the items inside the retaining assembly so that they cannot come into contact with each other or collide with the barrel walls or other parts that could cause damage during tumbling.

Fix the test samples into the two hexagonal flanges of the barrel, positioning them with the inside surface of sides or the back surface of fronts turned towards the rotation axis. Fit the samples so that they do not move. Fill any vacant positions with waste samples.

Sides shall be fitted into the holes in plates A and B, the silicone rubber sheets holding the sides firmly to prevent them from rotating in the assembly.

Spectacle fronts shall be mounted so that one of the lugs is inserted into the holes in plate B. It may be necessary to straighten the lug or twist the rim immediately either side of the lug so that the lug fits into the hole. The opposite lug should be firmly secured to plate A using adhesive tape. Alternatively, the spectacle fronts may be held to the plates using adhesive tape at both ends. Whatever method is used to fix spectacle fronts (e.g. using only adhesive tape), it is important to ensure that parts of the sample to be tested are not covered or protected.

### 4.5.3 Tumbling

After fitting the test samples between plates A and B, place the retaining assembly into the empty tumbling barrel (4.2.3.1), then fill the tumbling barrel to half its depth with the wear medium (4.2.3.5). Then fit the second silicone rubber sheet and plate C together with its retaining nut. Close the tumbling barrel and place it horizontally on the rotating system (4.2.3.2).

Rotate the tumbling barrel at a speed of (30 ± 2) rotations per minute for a total of 5 h ± 5 min. The direction of the rotation shall be reversed after 2,5 h ± 5 min.

NOTE After tumbling, it is permissible to leave the items in the barrel overnight.

### 4.6 Determination of nickel release

Remove the retaining assembly from the barrel and detach the items. Gently wipe off any remaining wear medium using a soft cloth or paper tissues.

Check the items for unexpected damage, e.g. test lenses fallen out of the fronts. If necessary and justified, exclude item(s) from further testing. Test the items for nickel release in accordance with Clause 5.

NOTE If only indicative information on the extent of nickel release is required, such information can be obtained by performing one of the tests specified in CEN/CR 12471.[4]

## 5 Method for the determination of nickel release

### 5.1 Principle

The parts to be tested for nickel release are placed in an artificial sweat test solution for one 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 (µg/cm$^2$/week).

### 5.2 Materials and reagents

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

**5.2.1 Deionized and aerated water**: fill a tall-form 2-l-beaker with deionized water, specific conductivity ≤ 1 µS/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 at least 150 ml/min. for 30 min.

**5.2.2 Sodium chloride**.

**5.2.3 DL-lactic acid**, $\rho$ = 1,21 g/ml, > 85 % (mass fraction).

**5.2.4 Urea**.

**5.2.5 Ammonia solution**, $\rho$ = 0,91 g/ml, 25 % (mass fraction).

**5.2.6 Dilute ammonia solution** [1 % (mass fraction)]: transfer 10 ml of ammonia solution (5.2.5) 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.

**5.2.7 Nitric acid**, $\rho$ = 1,40 g/ml, 65 % (mass fraction).

**5.2.8 Dilute nitric acid**, approximately 5 % (mass fraction): transfer 30 ml of nitric acid (5.2.7) into a 500 ml beaker containing 350 ml of deionized water (5.2.1). Stir and cool to room temperature. Transfer the solution to a 500 ml volumetric flask and make up to volume with deionized water.

**5.2.9 Degreasing solution**: dissolve 5 g of an anionic surface-active agent such as sodium dodecylbenzene sulfonate or sodium alkylaryl sulfonate, in 1 000 ml of water. An appropriately diluted, neutral, commercially available detergent may be used.

**5.2.10 Wax or lacquer**, suitable for electroplating purposes and 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 5.5 (see Annex A).

## 5.3 Apparatus

**5.3.1 A pH-meter**, accurate to ±0,02 pH.

**5.3.2 An analytical spectrometer**, capable of detecting a concentration of 0,01 mg nickel per litre and, after optimization, meeting the performance criteria given under a) and b). It is recommended that either an inductively coupled plasma - optical emission spectrometer or an electrothermal excitation atomic absorption spectrometer is used.

a) **Minimum precision**: the standard deviation of 10 measurements of the absorption of a full matrix calibration solution containing 0,05 mg/l of nickel shall not exceed 10 %;

b) **Limit of detection**: the limit of detection shall be considered to be 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.

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

**5.3.4 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 (see 5.4.1.1) 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 frame component to be tested.

In order to remove any trace of nickel, the container and holder shall be pretreated by being stored in a solution of dilute nitric acid (5.2.8) for at least 4 h. After acid treatment, rinse the container and holder with deionized water and dry.

## 5.4 Samples

### 5.4.1 Sample area

#### 5.4.1.1 Definition of sample area

Only the surface(s) of those parts of spectacle frames or sunglasses (hereinafter “frames”) liable to come into direct and prolonged contact with the skin[1)] shall be analysed. In this Technical Specification, such surfaces are defined as “sample area”.

#### 5.4.1.2 Determination of sample area

Determination of the sample area, *a*, in square centimetres, is achieved by marking the contour of the sample area defined in 5.4.1.1 (see Annex C). In order to achieve the required degree of analytical sensitivity, a minimum sample area of 0,2 $cm^2$ shall be tested. If necessary, identical items may be treated together to obtain this minimum area.

NOTE If a frame is being tested to ascertain its conformity with Directive 94/27/EC,[5] the accuracy with which the sample area of the frame or part has to be determined is dependent on the nickel release of this item. The closer the nickel release is to 0,5 µg/$cm^2$/week, the limit laid down in the Directive, the more accurately the surface area has to be determined.

1) See Clause 3 and ISO 12870 for guidance.

#### 5.4.1.3 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 5.4.2) by, for example, the application of one or more coatings of a wax or lacquer (5.2.10) which has been shown to protect from nickel release. 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 such unprotected surfaces shall be considered part of the sample area.

If, when non-significant surfaces are considered to be part of the sample area, the nickel release from the frame is found to be unacceptable, consideration should be given to masking the non-significant areas on a new frame and re-testing.

### 5.4.2 Sample preparation

Gently swirl the sample for 2 min in degreasing solution (5.2.9) at room temperature. Rinse thoroughly with deionized water and dry. After degreasing, the spectacle frame 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 sample. If there is a requirement to determine this nickel, the cleaning stage can be omitted. However, note that omission of this cleaning stage might itself affect the nickel release from the sample.

### 5.4.3 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).

## 5.5 Procedure

### 5.5.1 Preparation of the test solution

**5.5.1.1** The test solution representing the artificial sweat consists of deionized and aerated water (5.2.1) containing:

— 0,5 % (mass fraction) sodium chloride (5.2.2);

— 0,1 % (mass fraction) DL-lactic acid (5.2.3);

— 0,1 % (mass fraction) urea (5.2.4); and

— ammonia solution, 1 % (5.2.6).

**5.5.1.2** 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 1 000-ml beaker. Add 900 ml of freshly prepared deionized and aerated water and stir until all the added reagents are completely dissolved. Calibrate the pH-meter (5.3.1) in accordance with the manufacturer's instructions using freshly prepared buffer solutions. Immerse the pH electrode in the test solution. Stir gently and carefully add dilute ammonia solution until a stable value of (6,5 ± 0,1) pH is reached. Transfer the solution to a 1 000-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 6,4 to 6,6. Use the test solution within 3 h of preparation.

### 5.5.2 Release procedure

**5.5.2.1** Place the sample, suspended by its holder, in the test vessel (5.3.4). Add an amount of test solution corresponding to approximately 1 ml per $cm^2$ 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. 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 (5.3.3) at (30 ± 2) °C for 168 h without agitation.

If a reference disc (5.4.3) is to be determined, it should be suspended in 3 ml of test solution and treated in the same manner as a sample.

**5.5.2.2** After one week, remove the samples 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 volumetric flask (see Note below) washed with acid. In order to prevent redeposition of dissolved nickel, add dilute nitric acid (5.2.8) 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 5.3.2).

### 5.5.3 Determination of nickel

Determine the nickel content of the test solution using the analytical spectrometer (5.3.2).

### 5.5.4 Number of replicates

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

### 5.5.5 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.

## 5.6 Calculations

### 5.6.1 Nickel release

The nickel release of a sample, *d*, expressed in micrograms per square centimetre per week (µg/cm$^2$/week), is given by Formula (1):

$$d = \frac{V \times (C_1 - C_2)}{1\,000 \times a} \quad (1)$$

where

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

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

$C_1$ is the nickel concentration in the diluted test solution after one week, in micrograms per litre (µg/l);

$C_2$ is the mean value of the nickel concentration in the blank solutions after one week, in micrograms per litre (µg/l).

### 5.6.2 Interpretation of results

Multiply the result, *d*, established in 5.6.1 by 0,1 to obtain an adjusted analytical figure.

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

NOTE Due to the imprecision of the method specified in this Technical Specification, 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.

# 6 Test report

The test report for each determination shall include at least the following information:

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

b) the sampling procedure;

c) a reference to this Technical Specification, i.e. ISO/TS 24348:2014;

d) whether or not the accelerated wear procedure in Clause 4 was used;

e) a description of the sample area including the size of the sample area, expressed in square centimetres (cm$^2$);

f) the volume of test solution used;

g) for each replicate, the nickel release and its adjusted figure;

h) if relevant, details of any deviations from this standard method;

i) any unusual features observed during the determination;

j) the starting and completion dates of test;

k) identification of the laboratory carrying out the analysis;

l) the signature of the laboratory manager and the operator.

# Annex A
(informative)

# Statistical uncertainty of the test procedure and interpretation of results

Most chemical test methods are designed to measure the total amount of a substance in a material. This usually makes it possible to obtain an accurate result with close statistical agreement between laboratories because there is an absolute or true value.

To enable the restrictions on the use of nickel in the EC Nickel Directive (now REACH)[6] to be checked, the test method in this Technical Specification measures the rate of soluble nickel release from an item. With this type of chemical test, the result is dependent upon the specified conditions of test, and there is no absolute or true value. Consequently, it is more difficult to obtain close statistical agreement between laboratories when performing such migration (or release) tests.

This is illustrated by the statistical information obtained from a European interlaboratory trial of an earlier version of this method, carried out in 1993 in accordance with ISO 5725 (all parts).[1] Seven laboratories made determinations on two homogenous materials of known area with nickel release values of approximately 0,5 µg/cm$^2$/week and 1,5 µg/cm$^2$/week. Results were found to vary by up to 22 % within laboratories and by up to 45 % between laboratories. Moreover, these figures would be approximately three times higher if adjusted to give a 95 % confidence level (i.e. repeatability, $r$ = 0,33 µg/cm$^2$/week and reproducibility, $R$ = 0,68 µg/cm$^2$/week at the limit of 0,5 µg/cm$^2$/week).

This degree of uncertainty creates problems for manufacturers and enforcement authorities if test results are near the limit allowed in the EC Nickel Directive (now REACH).[6] In such cases, it is not statistically possible to pass or fail an item with any confidence. This inevitably leads to inconsistency in the interpretation of results.

There is no relationship between the total nickel content of a substance or preparation and its soluble nickel release under standard test conditions. Therefore, measuring the total nickel content and converting the result to give a nickel release figure is not a feasible answer to this problem.

The parameters which are most likely to affect nickel-release test results include: measurement of the surface area; effectiveness of degreasing agent and any “stopping-off”; temperature changes and composition of the artificial sweat, especially its oxygen content over the period of test; agitation or vibration of the sample; the surface area of the test area to volume of artificial sweat ratio; and the way the sample is suspended in the test solution. The incidence of surface defects also influences the test result.

Use of a certified reference material should improve the statistical agreement obtained between laboratories, but its use would lead to complications if relied upon to decide whether an item passes or fails at a value close to 0,5 µg/cm$^2$/week. The reference material should only be used as a quality control check (see Annex B).

A test procedure, such as the one described in this Technical Specification, which produces results varying by up to 120 % between laboratories ($C_{V,R}$ = 45 %) on homogenous materials of simple shape, would normally be considered technically unsuitable as a reference method. However, in reality, most items will either clearly pass or fail this test and only in relatively few cases will a result come within the area of uncertainty. When this occurs, it is important that laboratories interpret the results in the same way.

To achieve consistent interpretation of test results, an adjustment has been introduced into the standard. This adjustment is to be applied to all results, whatever instrumental technique has been used for the final determination. The statistical data above indicates that a factor of 0,4 would, under ideal conditions,

enable the test results of homogenous items of accurately known area and with an actual nickel release exceeding 0,5 µg/cm$^2$/week to be identified with a 95 % certainty that other proficient laboratories will concur. However, a general lack of experience in the analysis of items of commerce, together with difficulties in the measurement of surface area and in stopping-off "areas other than the sample area" justifies the application of a factor of 0,1 in the interpretation of the test result.

The analytical result is to be adjusted as described in 5.6.

# Annex B
(informative)

# Rules for production and preparation of reference material

For precise manufacture of the reference material, a minimum mass of 1 kg has to be alloyed. Gold (99,99 %), copper (99,9 %), nickel (99,9 %) and zinc (99,9 %) are weighed to an accuracy of ±0,1 g so as to achieve the following composition (see Table B.1 and Table B.2):

**Table B.1**

| Element | Content<br>% (mass fraction) |
|---|---|
| Au | 76,0 |
| Cu | 16,0 |
| Ni | 6,0 |
| Zn | 2,0 |

Alternatively, it is possible to use a pre-alloy with the following composition:

**Table B.2**

| Element | Content<br>% (mass fraction) |
|---|---|
| Cu | 66,7 |
| Ni | 25,0 |
| Zn | 8,3 |

and to weigh 24 % (mass fraction) of this pre-alloy together with 76 % (mass fraction) of gold.

After mixing, the metals have to be melted together in a ceramic crucible, preferably using an induction-heated furnace under vacuum or protective gas.

After homogeneous melting, the alloy is poured into a chill of cast-iron with a recommended thickness of 8 mm. After cooling to room temperature in air, the casting is cleaned by brushing with an alkaline degreasing solution. For homogenization of the alloy the casting then is annealed at 800 °C for 15 min under protective gas. After cooling to room temperature, the casting is cold rolled. The reduction rate should be as much as possible but 50 % minimum.

Homogeneity of the alloy shall be proved by analysing two samples from opposite ends and sides of the casting. Tolerances in the final composition should not exceed ±0,1 % of gold and ±0,2 % of copper, nickel and zinc, respectively.

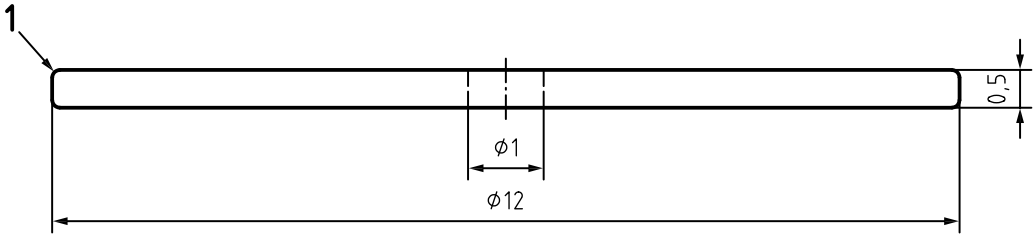
Intermediate annealing is carried out at 800 °C for 15 min under protective gas. After each annealing procedure the material is cooled down slowly from 800 °C to approximately 550 °C under protective gas (cooling rate approximately 50 °C/min) and subsequently quenched in water. For the last step of cold rolling, a reduction rate of approximately 70 % is necessary to reach a final thickness of 0,5 mm. Then, a last annealing procedure is necessary at 800 °C for 15 min. The Vickers hardness of the sheet at this final stage should be (190 ± 5) HV.

The surface of the sheet is abraded with wet emery paper No. 1200. Discs of the following shape and dimensions are punched out of the sheet and the edges rounded (see Figure B.1):

— diameter: (12,0 ± 1,0) mm;

— thickness: (0,5 ± 0,1) mm;

— centre hole diameter: (1,0 ± 0,2) mm.




**Key**

1 smooth edges

**Figure B.1 — Disc**

When tested according to this standard, the finished reference material should have an (unadjusted) nickel release of (0,4 ± 0,2) µg/cm$^2$/week.

**WARNING — All operations should be carried out so as to avoid contamination of the surface of the material with nickel. Discs may be used several times if, before each test for nickel release, they are abraded on each side with wet emery paper No. 600 followed by No. 1200 (see 5.4.3).**

# Annex C
(informative)

# Identification and determination of sample areaand coating of non-significant areas

## C.1 Identification and determination of sample area

When identifying the sample area, account should be taken of the elasticity of the skin and of the manner in which frames come into contact with the skin.

Where frames appear to be made from uniform material(s), consideration should be given to testing the whole surface (whether or not it is all in direct and prolonged contact with the skin) since errors might be introduced by the stopping-off process.

For articles made from round wire (diameter <3 mm) joined together, such as neck-chains or bracelets, the calculation of surface area should use the projected areas of all significant surfaces, unless the wire passes through the skin when the true surface is appropriate.

Frame parts made from square, rectangular, oval, etc. sections or round wire (diameter ≥3 mm) can be assumed to depress the skin around the part to a depth of 2 mm. Equally, if the surface of the part of the frame in contact with the skin contains indentations or depressions ≤2 mm, their projected areas should be included in the sample area.

The surface area of articles made essentially from sheet material, such as watch-cases, some medallions and lockets, can be assumed to be that area projected by all parts within 2 mm of the uncompressed skin-contact surface.

The designer of a frame may be able to advise on its surface area, especially when computer-aided design has been used.

Autocatalytic coating techniques may be applied to measure the surface area.

## C.2 Coating of non-significant areas

A number of stopping-off lacquers used in the electroplating industry have been suggested. The important points in their selection and use are:

— they are effective, preferably in a single coat, in preventing access of the artificial sweat to the non-significant surface;

— application is achieved using a brush and is followed by air drying;

— use of sufficient colour to enable their limits to be clearly visible and any deterioration during the test to be identified;

— they do not contaminate the artificial sweat or interfere with the release and analysis of nickel;

— they have a readily identified shelf life;

— they are safe in use;

— degreasing prior to application can be achieved simply and without chemical or physical alteration of the metallic surface.

# Annex D
(informative)

# Articles made from materials capable of releasing small amounts of nickel

Where the sample area of a frame or its part is composed of one homogeneous material, it may be assumed that the nickel release from the sample area of the frame is the same as that of the homogeneous material. Where the frame is composed of several metals/alloys, all of which have an adjusted nickel release of less than 0,5 μg/cm$^2$/week, there is a strong probability that the area of the frame in contact with the skin will also release less than 0,5 μg/cm$^2$/week of nickel, although it is necessary for the manufacturer to check in the first instance and periodically thereafter that this is the case.

However, there are a few instances in which the nickel release from such a composite might exceed the value of 0,5 μg/cm$^2$/week. It is therefore incumbent on the manufacturer to be aware of the situations in which this may occur. These include:

— the occurrence of bimetallic corrosion when a nickel-containing alloy is in electrical contact with a more noble metal/alloy in the sample area; examples are: a) contact of a stainless steel of marginal passivity, due to low chromium content or a high sulfur content, with a more noble metal/alloy such as gold, platinum or a higher alloyed stainless steel; b) brazing of a stainless steel with a silver-based alloy;

— change of surface condition as a result of welding, brazing, soldering or other heat treatment; or damage to the surface in the course of assembly;

— any degreasing, grinding or polishing operation that modifies the surface of the frame.

In calculating the value of nickel release for nickel-containing materials, for which homogeneous samples of uniform shape can be obtained, e.g. discs, it is necessary to multiply the observed value by 0,4 in order to compensate for variation in reproducibility and repeatability of the method. In calculating the value of nickel release from frames or their parts, it is necessary to multiply the observed value by 0,1 to take account of the above-mentioned variation and also errors that arise in “stopping-off” non-significant areas; in measurement of the areas that come into direct and prolonged contact the skin; and in the testing of non-uniform shapes.

Where coated samples representative of the materials used in the production of finished frames or their parts are to be tested, they shall be prepared at the same time as the frames or their parts that are to be placed on the market, using the same coating conditions, technique and solutions.

# Bibliography

[1] ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement methods and results*

[2] EN 12472, *Method for the simulation of wear and corrosion for the detection of nickel release from coated items*

[3] EN 16128, *Reference test method for release of nickel from those parts of spectacle frames and sunglasses intended to come into close and prolonged contact with the skin*

[4] CEN/CR 12471:2002, *Screening tests for nickel release from alloys and coatings in items that come into direct and prolonged contact with the skin*

[5] European Parliament and Council Directive 94/27/EC of 30 June 1994 amending for the 12th time Directive 76/769/EEC on the approximation of the laws, regulations and administrative provisions of the Member States relating to restrictions on the marketing and use of certain dangerous substances and preparations, OJ L 188, 22.7. 1994, pp. 1–2

[6] European Parliament and Council Regulation (EC) No 1907/2006 of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC

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