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Metallic and other inorganic coatings — Measurement of mass per unit area — Review of gravimetric and chemical analysis methods

Revêtements métalliques et autres revêtements inorganiques — Mesurage de la masse surfacique — Présentation des méthodes d'analyse gravimétrique et chimique

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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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This document was prepared by Technical Committee ISO/TC 107, *Metallic and other inorganic coatings*.

This second edition cancels and replaces the first edition (ISO 10111:2000), which has been technically revised. The following changes have been made:

a) a gravimetric method has been added for weighing the uncoated substrate and the finished sample;

b) the surface area increase caused by surface roughness has been considered to obtain a more realistic estimation of local geometric coating thickness (optional);

c) Annex A, which gives reagents for etching or stripping solutions, has been changed to informative as other solutions can be applied;

d) reagents in Annex A that referred to no longer existing standards or which contain hazardous chemicals have been removed;

e) outdated and uncited references in the Bibliography have been removed.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Metallic and other inorganic coatings — Measurement of mass per unit area — Review of gravimetric and chemical analysis methods

WARNING — The use of this document can involve hazardous materials, operations and equipment. It does not purport to address all of the safety or environmental problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel and the environment prior to application of this document.

1 Scope

This document gives guidelines for determining the average surface density over a measured area of anodic oxide or of a coating deposited autocatalytically, mechanically, by chemical conversion, by electrodeposition, by hot dip galvanizing and by chemical or physical vapour deposition using gravimetric and other chemical analysis procedures that have attained some degree of national or international standardization.

A variety of procedures are described and include:

— gravimetric procedures for chemical or electrochemical dissolution of the coating or the substrate to determine the coating surface density;

— gravimetric procedures for weighing the uncoated substrate and the coated (finished) specimen to determine the coating surface density;

— analytical procedures that utilize dissolution of the coating for determination of the coating surface density by instrumental chemical analysis methods.

With the exception of the gravimetric method as described in ISO 3892, this document does not give the measurement uncertainties of the methods cited.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2080, *Metallic and other inorganic coatings — Surface treatment, metallic and other inorganic coatings — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 2080 apply.

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

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

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

4 Principle

The mass of a coating over a measured area is determined by

a) weighing the test specimen before and after dissolving the coating in a reagent or electrolyte that does not attack the substrate, or

b) weighing the coating after dissolving the substrate in a reagent that does not attack the coating, or

c) dissolving both the coating and the substrate, or the coating alone, and quantitatively analysing the resulting solution, or

d) weighing the test specimen before and after the coating process, provided that the mass of the substrate material removed during those pre-treatment steps, after which a weighing would negatively affect the coating deposition steps, is negligible compared to the mass of the coating.

The surface density of the coating is calculated from the mass and area measurements. Its thickness is based on the mass, area and density of the coating material.

5 Special equipment

Certain specialized chemical, electrochemical and chemical analysis equipment is required for some of the specific methods referred to in Table A.1 (see Clauses 8 and 9).

6 Preparation of test specimen

6.1 Size

The specimen should be large enough to permit area and mass measurement of adequate accuracy (see Clauses 8 and 9).

6.2 Shape

The shape of the test specimen should be such that the surface area can be readily measured without difficulty. A rectangular or circular test specimen is usually suitable.

6.3 Edge condition

If the area to be measured is small and has to be known accurately, the edges may need to be dressed to remove smeared coating, to remove loose burrs and to provide well-defined and (for rectangles) straight edges. This should be considered for areas less than 100 mm^2.

One method of dressing the edges of a rectangular specimen involves clamping the specimen between two plastic or metal blocks with the edge of the specimen flush with the edges of the blocks and then grinding and polishing the edges metallographically.

6.4 Heat treatment

If the substrate has to be dissolved in such a way as to leave the coating intact, it may be desirable to first treat the test specimen so that the coating will not curl up tightly or fall apart. Some gold deposits of 1,5 mg/cm^2 (< 0,9 µm) will fall apart when their substrates are dissolved, but will support themselves after heat treatment at 120 °C for 3 h. If the thickness of a coating (instead of its surface density) is being determined, a heat treatment that could change the density of the coating material should not be used.

7 Measurement of coated area

7.1 Measurement method

Since the accuracy of the area measurement should be greater than the desired accuracy of the surface density measurement, the method of measuring the area depends on the desired accuracy and the specimen size.

7.2 Surface measuring equipment

7.2.1 Geometrical (projected) surface area

The area can be measured with a planimeter, but it is usually determined by linear measurements. Often a micrometre or vernier calliper is used. For large areas, however, a ruler may do.

For maximum accuracy, a measuring microscope should be used.

It may be difficult to measure directly the area of threaded articles with sufficient accuracy, in which case the area should be determined from drawings or published tables.

7.2.2 Surface area increase due to roughness (optional)

Surface roughness leads to an increase of the true surface area compared to the geometrical (projected) surface area as determined by the methods described in 7.2.1.

Using atomic force microscopy (AFM), confocal microscopy or interference microscopy and a suitable computer software, the relative surface area increase (RSAI) can be determined (at least for a small fraction of the total surface).

Enhance the geometrical (projected) surface by the RSAI to estimate the true surface area. Calculate the true surface density of the coating or the true coating thickness using this true surface area in order to obtain a better agreement with geometrical coating thickness measurements in cross-section.

The RSAI should be determined on the uncoated substrate before any coating is applied as some coatings tend to level surface roughness, but preferably after pre-treatment steps, which increase surface roughness, e.g. to improve adhesion.

7.3 Number of measurements

Because circular or rectangular specimens will not be perfectly circular or rectangular, each dimension should be measured in three places. For a rectangle, the length of each edge and the length and width through the centre should be measured and an average obtained for each dimension.

NOTE In the case of a cylinder, one would normally measure the diameter and length. In specifications for metallic coated wire (fencing) that has been electroplated or coated by other processes, the length of the wire specimen is not measured, but is, in effect, calculated from the mass (which is measured anyway), the radius and the density of the substrate material as follows:

$$l = \frac{m}{\pi r^2 \rho_s}$$

where

l is the length;

m is the mass;

r is the radius;

ρ_s is the density of the substrate.

8 Determination of mass of coating by chemical analysis

8.1 General

The chemical analysis method is very general. Both coating and substrate or the coating alone are dissolved in a suitable reagent (see Annex A for examples) and then the resulting solution is analysed for the coating material. For each coating-substrate-reagent combination, there may be several analytical methods, e.g. photometric or volumetric methods, atom absorption spectroscopy or inductively coupled plasma with optical emission or mass spectrometry.

8.2 Restrictions

The chemical analysis method cannot be used when the coating material cannot be completely removed from the substrate material by chemical means or when there is a constituent common to both that is not readily separated (e.g. nickel phosphorus alloy on nickel).

9 Gravimetric determination of mass of coating

9.1 Specimen size

Since the measurement uncertainty of the mass measurement should be less than the desired measurement uncertainty of the surface density measurement, the test specimen should be large enough for the coating to be weighed with the desired accuracy (see 9.2).

9.2 Limitations

In principle, the gravimetric procedures can be used to measure very thin coatings or to measure coatings over small areas, but not thin coatings over small areas. The limits depend on the required accuracy, e.g. 2,5 mg/cm^2 of coating might require 1 cm^2, but 0,1 mg/cm^2 of coating would require 25 cm^2 to obtain 2,5 mg of coating.

The gravimetric method does not indicate the presence of bare spots or sites with thicknesses lower than the specified minimum in the measuring areas. In addition, the single value obtained from each measuring area is the mean thickness of that area.

The measurement uncertainty of the gravimetric method is normally less than 5 % over a wide range of thicknesses (see ISO 3892).

9.3 Restrictions

The gravimetric procedures can be used for many coating–substrate combinations. Except for the procedure described in 9.5.4, they cannot be used where neither the coating nor substrate material can be completely removed, one from the other by chemical or physical means.

9.4 Gravimetric analysis equipment

A balance is required for gravimetric analysis, but the required sensitivity of the balance depends on the size of the test specimen, the coating thickness (coating mass) and the required accuracy of the measurement. The analytical balance should be capable of weighing to an accuracy of 0,1 mg for weighing the test pieces under examination before and after dissolution of the coatings or before and after the coating process, respectively.

For anodic and cathodic dissolution, a (constant) direct current source is necessary.

9.5 Procedure

9.5.1 General

The mass of coating may be determined by

a) weighing the test specimen before and after dissolving the coating (see Annex A for exemplary reagents) and taking the difference (see 9.5.2), or

b) dissolving the substrate (see Annex A for exemplary reagents) and weighing the coating directly (see 9.5.3), or

c) weighing the test specimen before and after deposition of the coating and taking the difference (see 9.5.4).

The first time a gravimetric method is used, it should be evaluated in accordance with 9.5.2.2 and 9.5.3.2.

9.5.2 Difference method with dissolution of the coating

9.5.2.1 First, clean the test specimen of any foreign material, then rinse it with alcohol (methanol, ethanol, isopropanol) or another suitable solvent, blow it dry with clean air and weigh it. Immerse the specimen in the appropriate reagent (see Annex A for examples) to dissolve the coating either chemically or electrochemically, rinse it with water, then with alcohol, blow it dry with clean air and weigh it again. The loss of mass is the mass of the coating.

9.5.2.2 To determine if any dissolution of the substrate has occurred, repeat the process with the stripped substrate, making sure that the substrate is immersed in the reagent for the same length of time as before. Any loss of mass enables one to make a judgement of a possible error due to any dissolution of the substrate with the coating during the stripping process.

9.5.3 Direct weighing method with dissolution of the substrate

9.5.3.1 Dissolve the substrate in the appropriate reagent (see Annex A for examples). Rinse the coating with water and then alcohol (methanol, ethanol, isopropanol) or another suitable solvent, blow it dry with clean air and weigh it.

9.5.3.2 To determine if any dissolution of the coating occurred, submit the isolated coating to the same stripping process, making sure that the coating is immersed in the stripping reagent for the same length of time as it was during the stripping process. Any loss of mass enables one to make a judgement of a possible error due to any dissolution of the coating with the substrate during the stripping process.

9.5.4 Difference method without dissolution

First, clean the uncoated test specimen of any foreign material, rinse it with alcohol or another suitable solvent, which does not attack the substrate material nor disturb the subsequent coating process, blow it dry with clean air and weigh it.

Then subject the uncoated test specimen to the coating process.

Afterwards, clean the coated test specimen of any foreign material, rinse it with alcohol or another suitable solvent, which attacks neither the coating nor uncovered zones of the substrate, blow it dry with clean air and weigh it.

The gain of mass is the mass of the coating.

As many of the required pre-treatment steps for the substrate material as possible should be done before the first weighing, especially when they remove substrate material. However, pre-treatment

steps, which are integral part of the coating process and do not allow for an interruption for weighing, e.g. wet in wet or without breaking the vacuum, cannot be done before weighing. When such pre-treatment steps remove substrate mass, which is a significant fraction or even a multiple of the coating mass, the method described in this subclause cannot be applied.

10 Calculations

10.1 Surface density

Calculate the surface density, ρ_A, in milligrams per square centimetre, from Formula (1):

$$\rho_A = \frac{m}{A} \tag{1}$$

where

m is the mass of coating, in milligrams;

A is the area, in square centimetres.

10.2 Thickness

Calculate the thickness, d, in micrometres, from Formula (2):

$$d = 10 \times \frac{\rho_A}{\rho_c} \tag{2}$$

where

ρ_A is the surface density, in milligrams per square centimetre;

ρ_c is the density of the coating in grams per cubic centimetre.

NOTE The density of a coating metal is usually not the same as the published values of bulk or wrought metal. For example, the density of electrodeposited gold is generally less than 19,3 g/cm^3 and sometimes as low or lower than 17 g/cm^3.

If there is any uncertainty about the numerical value of the density used to calculate the thickness in micrometres from the surface density in milligrams per square centimetre, the density value used should be stated.

Annex A
(informative)

Reagents for selective dissolution of metal layers

The stripping methods cited in Table A.1 are described in specifications, in the open literature, or have been used routinely by at least one laboratory.

With many of the reagents given in Table A.1, there may be some dissolution of the layer other than the one being stripped. Often the dissolution is not significant, but the possibility should be tested for as described in 9.5.2 and 9.5.3.

Dissolution is carried out at room temperature unless otherwise indicated. All test pieces are rinsed and dried before weighing.

Table A.1 — Reagents for selective dissolution of metallic and other inorganic coatings using both chemical and electrochemical methods

Coating	Substrate	Reagents[a]	Comments
Aluminium	Steel	(1) 20 parts by mass NaOH + 80 parts water (2) concentrated HCl	See ASTM A428M-10(2014). Immerse for a few minutes (avoid a longer time) at about 90 °C. While rinsing, scrub with a sponge to remove loose material. Drain off water, immerse for 3 s in concentrated HCl at room temperature, scrub again in running water, repeat the entire process until there is no visible reaction in HCl. Two or three cycles are required normally.
Cadmium	Steel	300 g/l NH_4NO_3	See ISO 2082:2017. Immerse.
Cadmium	Steel	200 g Sb_2O_3 in 1 l concentrated HCl	See Reference [16]. Immerse till evolution of gas practically stops.
Cadmium	Steel	20 g Sb_2O_3 in 800 ml concentrated HCl + 200 ml water	Immerse till evolution of gas practically stops.
Cadmium	Steel	5 % $(NH_4)_2S_2O_8$ + 10 % by volume of concentrated NH_4OH solution	See Reference [16]. Immerse.
Chromate	Aluminium	(1) $NaNO_2$ (2) 1 part by volume water + 1 part concentrated HNO_3	See ASTM B449-93 (2015). Immerse in molten $NaNO_2$ at 326 °C to 354 °C for 2 min, rinse in cold water, then in reagent (2) for 30 s at room temperature.

[a] The relative densities at 20 °C (ρ_{20}) of the acids referred to in this table are as follows:

— hydrochloric acid HCl, 1,18;

— nitric acid HNO_3, 1,42;

— phosphoric acid H_3PO_4, 1,75;

— sulfuric acid H_2SO_4, 1,84.

[b] EDTA = ethylene diaminetetraacetic acid.

Table A.1 *(continued)*

Coating	Substrate	Reagents[a]	Comments
Chromate (aged)	Aluminium and its alloys	(1) 98 % $NaNO_3$ + 2 % NaOH solution (2) 1 part by volume 65 % to 70 % mass fraction HNO_3 + 1 part water	See ISO 3892:2000. Immerse in (1) for 2 min to 5 min at 370 °C to 500 °C (some coatings may require the higher temperature). Rinse in water, immerse in (2) for 15 s to 30 s at room temperature.
Chromate (fresh)	Aluminium alloys	1 part by volume water + 1 part 65 % to 70 % mass fraction HNO_3	See ISO 3892:2000. Immerse for 1 min at room temperature within 3 h of application of coating.
Chromate (aged and fresh)	Aluminium alloys	(1) 500 ml 1 % H_2SO_4 (2) $(NH_4)_2S_2O_8$	See EN 12487:2007. Immerse in (1) for 10 min at boiling point, evaporate to about 50 ml. Treat with (2) (concentration not critical) to oxidize Cr(III) to Cr(VI). Determine photometrically at wavelength (λ) = 445 nm.
Chromate	Tin or zinc	(1) 100 g KNO_3 + 100 g KCl in 1 l of water (2) 100 g NaCl or KCl in 1 l of water	Immerse chromates on tin in (1), rinse, dry and determine gravimetrically or volumetrically. Immerse chromates on zinc in (2), rinse, dry and determine gravimetrically or volumentrically.
Chromium	Nickel or steel	12 g/l NaOH	See Reference [14]. Chromium dissolves anodically at about 20 mA/cm^2.
Copper	Zinc alloys	1 part concentrated HCl + 4 parts water	Dissolves zinc alloy substrate. Cool initial reaction to prevent dissolution of copper.
Gold	Steel, copper, nickel or Fe-Ni-Co	1 to 3 parts by volume water + 1 part concentrated HNO_3	Substrate dissolved by immersion. Heat as required. Keep free of halides. Nickel may passivate - make contact with nickel wire to increase area of nickel.
Lead-tin alloys	Steel		See “terne plate”.
Nickel	Brass	90 % H_3PO_4	Immerse at 180 °C to 190 °C, do not add water. 2,5 µm nickel dissolve in about 10 min.
Nickel or nickel over copper	Zinc alloys	1 part concentrated HCl + 4 parts water	See Reference [15]. Dissolves zinc alloy substrate. Cool initial reaction to prevent dissolution of copper. Check for dissolution of nickel.
Phosphate (amorphous)	Aluminium and its alloys	1 part by volume water + 1 part 65 % to 70 % mass fraction HNO_3	See ISO 3892:2000. Immerse for 1 min at room temperature.
Phosphate (crystalline)	Aluminium and its alloys	65 % mass fraction HNO_3 + 35 % mass fraction H_2O	See ISO 3892:2000. Immerse 5 min at 75 °C, or 15 min at room temperature.

[a] The relative densities at 20 °C (ρ_{20}) of the acids referred to in this table are as follows:

— hydrochloric acid HCl, 1,18;

— nitric acid HNO_3, 1,42;

— phosphoric acid H_3PO_4, 1,75;

— sulfuric acid H_2SO_4, 1,84.

[b] EDTA = ethylene diaminetetraacetic acid.