International Standard 4524/1

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings — Part 1 : Determination of coating thickness

Revêtements métalliques — Méthodes d'essai des dépôts électrolytiques d'or et d'alliages d'or — Partie 1 : Détermination de l'épaisseur du dépôt

First edition — 1985-03-15

UDC 669.218.7 : 531.717 **Ref. No. ISO 4524/1-1985 (E)**

Descriptors : coatings, metal coatings, electrodeposited coatings, gold plating, decorative coatings, protective coatings, tests, determination, thickness.

Price based on 5 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 4524/1 was prepared by Technical Committee ISO/TC 107, *Metallic and other non-organic coatings*.

Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings — Part 1 : Determination of coating thickness

1 Scope and field of application

This part of ISO 4524 specifies methods for the determination of the thickness of electrodeposited gold and gold alloy coatings for engineering, and decorative and protective purposes.

2 References

ISO 1463, *Metallic and oxide coatings — Measurement of coating thickness — Microscopical method.*

ISO 2177, *Metallic coatings — Measurement of coating thickness — Coulometric method by anodic dissolution.*[1]

ISO 3497, *Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods.*

ISO 3543, *Metallic and non-metallic coatings — Measurement of thickness — Beta backscatter method.*

ISO 3868, *Metallic and other non-organic coatings — Measurement of coating thicknesses — Fizeau multiple-beam interferometry method.*

ISO 4518, *Metallic coatings — Measurement of coating thickness — Profilometric method.*

ISO 4524/4, *Metallic coatings — Test methods for electrodeposited gold and gold alloy coatings — Part 4 : Determination of gold content.*

3 General

The methods given in this part of ISO 4524 are those which are considered to have an adequate accuracy when properly used with test specimens for the particular method. If a referee method is required, it shall be agreed between the parties concerned and shall be selected from the test methods given in clauses 4 to 11. The method chosen shall be one which will yield the most reliable results considering such factors as expected coating thickness, shape of components, size of components, coating material, basis material, etc. In those methods requiring a value for the density of the electrodeposited coating the true density of the gold or gold alloy should be used. If the true density of the gold alloy deposit is not known, use a suitable arithmetically calculated value; for example a 60 % (m/m) gold and 40 % (m/m) silver alloy coating would have a calculated density, ϱ, expressed in grams per cubic centimetre, of

$$\frac{100}{\frac{60}{19,3} + \frac{40}{10,5}} = 14,5$$

Otherwise, use the value 19,3 g/cm^3.

A value for the density is required for coulometric, X-ray, spectrometric, beta backscatter, gravimetric and chemical analysis methods. In these cases, if a density is calculated or assumed, the accuracies given may not be obtainable.

Other test methods may be used if it can be demonstrated that they have a measurement uncertainty of less than 10 %, or that they are as good as or better than the methods given in this part of ISO 4524 for the particular application.

The supplier of a proprietary gold electroplating solution can generally estimate the density of the gold deposited from that solution, but variations can arise due to different operating conditions, ageing of the electrolyte, poor bath maintenance or inclusions of organic matter.

The approximate density of an alloy deposit may be calculated arithmetically provided that its composition is known. How-

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[1] At present at the stage of draft. (Revision of ISO 2177-1972.)

ever, the use of this method may produce large errors, as illustrated in table 1.

The values in table 1 are intended to illustrate typical densities of gold electrodeposits produced by commonly used electrolytes. The values are for guidance only and are not to be used as density factors when converting from mass per unit area to deposit thickness.

Table 1 — Variation of deposit purity and density

Type	Deposit purity [% (m/m)]	Density* (g/cm^3)
Alkaline cyanide (matte)	99,999	18,9
Alkaline non-cyanide (bright)	99,955	19,2
"Alloy" (Ag) alkaline cyanide (bright)	99,020	16,7
"Alloy" (Cd) alkaline non-cyanide (bright)	98,576	18,9
Acid hard gold (Co) (bright)	99,905	17,8

* Values given for guidance which cannot be used as density factors when converting from mass per unit area to deposit thickness.

4 Microscopical method

Use the method specified in ISO 1463. This method is considered to have a measurement uncertainty of less than 10 % or ± 0,8 µm, whichever is the greater value. With high resolution microscopes and careful preparation of the test specimens, measurement uncertainties of less than 0,5 µm can be achieved.

5 Beta backscatter method

Use the method specified in ISO 3543. This method is considered to have a measurement uncertainty of less than 10 % for thicknesses of gold corresponding to a mass per unit area equal to or greater than 1 mg/cm^2 on substrates with an atomic number of less than 35.

6 Gravimetric method

6.1 Principle

Chemical or electrochemical dissolution of the substrate (without attack of the gold coating). Calculation of the average thickness over a small area from the area, mass and density of the coating.

6.2 Test specimen

Carefully punch or cut a test specimen from the article such that the area of gold can be measured to an accuracy of 2 % or better, and the mass of gold can be determined subsequently to an accuracy of 2 % or better. It may be necessary to square off and sand the edges to remove gold smeared over the edge by the cutting operation.

6.3 Procedure

Measure the area of coating to an accuracy of 2 % or better.

Remove as much as possible of the basis material by mechanical means before stripping in order to minimize potential attack on the coating. Dissolve the substrate material without attacking the coating. For many substrates, nitric acid ($\varrho \approx 1{,}42$ g/ml) diluted 1 + 3 with water may be used at approximately 20 °C, but this acid may dissolve some of the alloying elements in the case of some alloy coatings.

Remove the gold, dry at 100 °C for approximately 30 min, and weigh to an accuracy of 2 % or better. If the gold breaks up into small pieces, it may be necessary to filter and weigh the residue by normal analytical techniques.

6.4 Expression of results

The average coating thickness, d, in micrometres, is given by the equation

$$d = \frac{10\,m}{A\,\varrho}$$

where

m is the mass, in milligrams, of the coatings;

A is the area, in square centimetres, of the gold-plated surface of the specimen;

ϱ is the density, in grams per cubic centimetre, of the coating (see clause 3).

7 Chemical analysis

7.1 Principle

Removal of the basis material from a small known area (the test specimen) of the article, taken from a desired point. Dissolution of the gold in aqua regia. Spectrophotometric or atomic absorption spectrometric determination of the mass of gold in the test solution and hence on the test specimen. Calculation of the average thickness of the gold coating on the test specimen from its area, the mass of gold and from density and purity of the gold coating.

NOTE — If the gold content is to be determined, the washed and dried coating should be weighed before dissolution in aqua regia.

7.2 Reagents

Use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

7.2.1 Nitric acid, $\varrho \approx 1,2$ g/ml, about 25 % (m/m) solution.

7.2.2 Aqua regia.

Add 25 ml of concentrated nitric acid ($\varrho \approx 1,42$ g/ml) to 75 ml of concentrated hydrochloric acid ($\varrho \approx 1,18$ g/ml). Prepare just before use.

7.2.3 Gold, stock standard solution, corresponding to 0,050 g of Au per litre.

Dissolve 0,050 g of "proof" gold, purity 99,99 % (m/m) in 20 ml of the aqua regia (7.2.2) and dilute with water to the mark in a one-mark volumetric flask of capacity 1 000 ml.

1 ml of this standard solution contains 50 µg of Au.

7.3 Apparatus

Thoroughly clean all glassware, including the spectrophotometer cells, with the aqua regia (7.2.2) and rinse with water before use. It is preferable to reserve glassware solely for use with these analyses.

7.4 Test specimen

Carefully punch or cut a test specimen from the article so that its area can be measured to an accuracy of 2 % or better and so that the mass of gold can be determined subsequently to an accuracy of 2 % or better. It may be necessary to square off and sand the edges to remove any gold smeared over the edge by the punching or cutting operation.

The accuracy of the thickness measurements depends largely on the accuracy with which the area of the test specimen is measured. For articles of thin cross-section, accurately sized test specimens may be taken conveniently by using a punch and die to give discs of known diameter. For gold electroplated pads on printed wiring boards, the copper foil can usually be detached mechanically. If necessary, the pads can be detached from the laminate by boiling in a 200 g/l sodium hydroxide solution.

The quantities of reagents and the dilutions specified in the following procedures are related to an area of 0,1 cm^2, which is the smallest test specimen that should be taken. If larger areas are taken, adjust the dilutions and the volumes of the aliquot portions of the test solution accordingly.

7.5 Preparation of test and standard solutions

7.5.1 Test solution

Remove as much as possible of the basis material from the test specimen (7.4) by mechanical means before stripping, in order to minimize potential attack on the gold coating. Separate the coating from the remaining basis material by dissolving the latter in the nitric acid solution (7.2.1). Wash and dry the stripped coating and dissolve it in 3 ml of the hot aqua regia (7.2.2) in a beaker of capacity 50 ml.

7.5.2 Standard solutions

Into a series of six of the 50 ml beakers, (7.6.3.2) place the volumes of the gold standard solution (7.2.3) shown in table 2.

NOTE — For lower ranges of thickness, dilute the standard gold solution fivefold.

7.6 Spectrophotometric method

7.6.1 Principle

Addition of potassium chloride to the test solution to give stable gold potassium chloride. Evaporation to dryness and spectrophotometric determination of the gold content.

Table 2 — Standard solutions

Volume of standard gold solution (7.2.3)	Corresponding mass of gold	Concentration of gold in final solution
ml	mg	mg/ml
0*	0*	0*
1,0	0,05	0,005
2,0	0,10	0,010
4,0	0,20	0,020
6,0	0,30	0,030
8,0	0,40	0,040

* Compensation solution.

Basis metals that have soluble colourless chlorides, and copper, nickel, cobalt and iron that have coloured chlorides, do not interfere. The method is, therefore, suitable for gold coatings containing such metals. In the case of gold coatings containing alloying metals, such as silver, that have insoluble chlorides, it may be necessary to filter the solution before measuring the absorbance.

7.6.2 Reagents

7.6.2.1 Potassium chloride, 10 g/l solution.

7.6.2.2 Hydrochloric acid.

Dilute 200 ml of concentrated hydrochloric acid ($\varrho \approx 1{,}18$ g/ml) to 1 000 ml.

7.6.3 Apparatus

Ordinary laboratory apparatus and

7.6.3.1 Spectrophotometer, fitted with silica cells of 10, and 40 or 50 mm optical path lengths. The instrument is fitted with a monochromator, not a filter.

7.6.3.2 Beakers, 50 ml capacity, squat form. At least six are required.

7.6.3.3 Microfilter funnel, fitted with a sintered glass filter plate or a suitable filter stick.

7.6.3.4 Electric oven, capable of being maintained at 110 ± 2 °C.

7.6.4 Preparation of calibration graph

7.6.4.1 Preparation of calibration solutions

Treat the contents of each beaker of dilute gold standard solution (7.5.2) as follows. Add 1 ml of the potassium chloride solution (7.6.2.1), evaporate carefully to incipient dryness on a hotplate or water-bath, dry in the oven (7.6.3.4), maintained at 110 ± 2 °C, and allow to cool. Redissolve the residue in the hydrochloric acid (7.6.2.2) and dilute to the mark with the same acid in a one-mark volumetric flask of capacity 10 ml.

7.6.4.2 Spectrophotometric measurements

Carry out the spectrophotometric measurements of the calibration solutions (7.6.4.1) in the spectrophotometer (7.6.3.1) at a wavelength of 312 nm and using 10 mm cells, after having adjusted the instrument to zero absorbance against water.

7.6.4.3 Plotting the calibration graph

Deduct the absorbance of the compensation solution (see table 2) from those of the other calibration solutions. Plot a graph of the concentrations, in milligrams of gold per millilitre, as abscissae against the corresponding net values of absorbance as ordinates. A straight line should be obtained.

7.6.5 Determination

Carry out the determination in duplicate, starting from two different test specimens (7.4). Add 1 ml of the potassium chloride solution (7.6.2.1) to the test solution (7.5.1) and evaporate carefully to incipient dryness on a hotplate or water-bath. Dry in the electric oven (7.6.3.4), maintained at 110 ± 2 °C and allow to cool. Redissolve the residue in the hydrochloric acid (7.6.2.2) in a one-mark volumetric flask of capacity indicated in table 3, and dilute to the mark with the same acid.

Table 3 — Volumes of dilution and cell sizes for various thicknesses of coating

Approximate coating thickness	Capacity of one-mark volumetric flask	Cell size
µm	ml	mm
$5{,}0 < d \leqslant 10{,}0$	20	10
$1{,}25 < d \leqslant 5{,}0$	10	10
$0{,}1 \leqslant d \leqslant 1{,}25$	10	40

Measure the absorbance of the solution in the spectrophotometer (7.6.3.1) at a wavelength of 312 nm and using the appropriate cell indicated in table 3, after having adjusted the instrument to zero absorbance against the blank test solution (7.6.6).

By means of the calibration graph, determine the mass of gold corresponding to the spectrophotometric measurement, taking into account the blank test (7.6.6).

7.6.6 Blank test

Carry out a blank test in parallel with the determination, by the same procedure and using the same quantities of all the reagents, but omitting the test specimen.

7.7 Atomic absorption spectrometric method

7.7.1 Principle

Addition of lanthanum chloride to the test solution to suppress interferences and measurement of the atomic absorption.

7.7.2 Reagent

7.7.2.1 Lanthanum chloride, approximately 100 g/l solution.

Dissolve approximately 58,6 g of lanthanum oxide in 250 ml of concentrated hydrochloric acid ($\varrho \approx 1{,}18$ g/l) and dilute to 500 ml with water.

7.7.3 Apparatus

Ordinary laboratory apparatus and

7.7.3.1 Atomic absorption spectrometer.

7.7.4 Preparation of calibration graph

7.7.4.1 Preparation of calibration solutions

Treat the contents of each beaker of dilute gold standard solution (7.5.2) as follows. Transfer to a series of six one-mark volumetric flasks of capacity 100 ml, add 4 ml of the lanthanum chloride solution (7.7.2.1) and dilute to the mark with water.

7.7.4.2 Spectrometric measurements

Aspirate the calibration solutions (7.7.4.1) directly into the flame of the atomic absorption spectrometer (7.7.3.1), using the conditions for gold determination specified by the instrument manufacturer, and record the absorbance readings.

7.7.4.3 Plotting the calibration graph

Deduct the absorbance of the compensation solution from those of the other calibration solutions. Plot a graph of the concentrations, in milligrams of gold per millilitre, as abscissae against the corresponding net values of absorbance as ordinates.

7.7.5 Determination

Transfer the test solution (7.5.1) to a one-mark volumetric flask of capacity indicated in table 4, add the indicated volume of the lanthanum chloride solution (7.7.2.1) and dilute to the mark with water.

Table 4 — Volumes of dilution and of lanthanum chloride solution for various masses of gold

Mass of gold in test specimen	Capacity of one-mark volumetric flask	Volume of lanthanum chloride solution (7.7.2.1)
mg	ml	ml
$m_{Au} \leqslant 0{,}2$	10	0,4
$0{,}2 < m_{Au} \leqslant 2$	100	4
$2 < m_{Au} \leqslant 20$	1 000	40

Measure the absorbance of the resultant solution as described in 7.7.4.2.

By means of the calibration graph, determine the mass of gold corresponding to the spectrophotometric measurement, taking into account the blank test (7.7.6).

7.7.6 Blank test

Carry out a blank test in parallel with the determination, by the same procedure and using the same quantities of all the reagents but omitting the test specimen.

7.8 Expression of results

The average coating thickness, d, in micrometres, is given by the equation

$$d = \frac{10\, m_1}{A\, \varrho} \times \frac{100}{w_{Au}}$$

where

m_1 is the mass, in milligrams, of gold in the test solution, calculated from the calibration graph (7.6.4 or 7.7.4) and the total volume of the final test solution (see tables 3 and 4) and taking into account the blank test (7.6.6 or 7.7.6);

A is the area, in square centimetres, of the test specimen (7.4);

ϱ is the density, in grams per cubic centimetre, of the coating (see clause 3);

w_{Au} is the gold content, expressed as a percentage by mass, of the coating (see ISO 4524/4).

8 X-ray spectrometric method

Use the method specified in ISO 3497. This method is considered to have a measurement uncertainty of less than 10 % over the range of 0,5 to 7,5 µm.

9 Profilometric method

Use the method specified in ISO 4518. This method is considered to have a measurement uncertainty of less than 10 %.

10 Interferometric method

Use the method specified in ISO 3868. This method is considered to have a measurement uncertainty of less than 10 %.

11 Coulometric method

Use the method specified in ISO 2177, with an electrolyte recommended by the instrument manufacturer for the particular coating/substrate combination.

12 Test report

The test report shall include at least the following information :

a) a reference to this part of ISO 4524, including an identification of the specific method used;

b) the result(s) of the test(s) carried out and the form in which these are expressed;

c) any unusual features noticed during the determination;

d) any operation not included in this part of ISO 4524 or in the International Standards to which reference is made;

e) any other relevant information requested by the purchaser.