# INTERNATIONAL STANDARD

**ISO 3497**

# Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods

*Revêtements métalliques — Mesurage de l'épaisseur — Méthodes par spectrométrie de rayons X*

First edition — 1976-02-01

UDC 669.058 : 531.717 : 539.26

Ref. No. ISO 3497-1976 (E)

Descriptors : metal coatings, tests, dimensional measurement, thickness, spectrophotometric analysis, ray analysis.

Price based on 7 pages

## FOREWORD

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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.

International Standard ISO 3497 was drawn up by Technical Committee ISO/TC 107, *Metallic and other non-organic coatings*, and circulated to the Member Bodies in August 1974.

It has been approved by the Member Bodies of the following countries :

| | | |
|---|---|---|
| Czechoslovakia | Italy | Sweden |
| France | Mexico | Switzerland |
| Germany | Poland | Turkey |
| Hungary | Portugal | United Kingdom |
| India | Romania | U.S.A. |
| Ireland | South Africa, Rep. of | U.S.S.R. |
| Israel | Spain | |

No Member Body expressed disapproval of the document.

# Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods

## 1 SCOPE AND FIELD OF APPLICATION

**1.1** This International Standard specifies procedures for measuring the thickness of metallic coatings by the use of X-ray spectrometric methods.

**1.2** This International Standard is applicable to the determination of the mass of coating per unit area as well as the coating thickness.

**1.3** The general principles presented here are applicable to the determination of the thickness of most metallic coatings on any substrate, metallic or non-metallic (see 3.4 and 3.5). The maximum measurable thickness for a given coating is that thickness beyond which the intensity of the characteristic secondary X-radiation is no longer sensitive to small changes in thickness.

**1.4** Problems of personnel protection against X-rays are not covered by this International Standard. For information on this important aspect, reference should be made to current documents of ISO, national documents and local regulations, if such exist.

## 2 PRINCIPLE

### 2.1 Excitation

The measurement of the thickness of coatings by X-ray spectrometric methods is based on the combined interaction of the coating and substrate with an intense beam of polychromatic X-radiation. This interaction results in the generation of discrete wavelengths of secondary radiation characteristic of the elements composing the coating and substrate.

### 2.2 Dispersion

By means of a single-crystal spectrometer, a selected wavelength characteristic of either the coating or the substrate is separated for individual measurement.

### 2.3 Detection

The intensity of the selected wavelength is measured by means of an appropriate radiation detector in conjunction with electronic pulse-counting circuitry (scaler). Intensities may be expressed in terms of "counts per second", although it is often more convenient to express intensity in terms of the total counts accumulated in a "fixed-time" scaling period.

### 2.4 Basic principle

A relationship exists between coating thickness and secondary radiation intensity up to the limiting thickness mentioned in 1.3. Both of the techniques described are based on the use of primary standards of known coating thickness which serve to correlate quantitatively the radiation intensity and thickness.

### 2.5 Thickness measurements by X-ray emission

In this technique, the spectrometer is positioned to record the intensity of a prominent wavelength characteristic of the coating metal, for example Ni K$\alpha$, Au L$\alpha$ 1, etc. The intensity at this wavelength will be at a minimum for a sample of the bare substrate, where it consists only of scattered (background) radiation. For a thick sample of the solid coating metal, or for an electroplated sample having a greater than "infinite" coating thickness (see 1.3), the intensity will have its maximum value for a given set of conditions. For a sample having a coating of less than "infinite" thickness, the intensity will have an intermediate value. The intensity of the emitted secondary X-radiation depends in general upon the excitation energy, the atomic numbers of the coating and substrate, the area of the specimen exposed to the primary radiation, and the thickness of the coating. If all of the other variables are fixed, the intensity or the characteristic secondary radiation is a function of the thickness or mass per unit area of the coating. The exact relationship between the measured intensity and the corresponding coating thickness shall be established by the use of standards having the same coating and substrate compositions as the samples to be measured. The maximum thickness that can be measured by this method is somewhat less than what is, effectively, "infinite thickness". This limiting thickness depends, in general, upon the atomic number of the coating and the radiation energy. The typical relationship between a coating thickness and the intensity of a characteristic emission from the coating metal is illustrated by the curve in figure 1.

### 2.6 Thickness measurements by X-ray absorption

In this technique the spectrometer is positioned to record the intensity of a selected wavelength emitted by the basis material. The intensity will be a maximum for a sample of the bare basis material and will decrease with increasing coating thickness. This is because both the exciting and secondary characteristic radiations undergo attenuation in passing through the coating. Depending upon the atomic

number of the coating, when the coating thickness is increased to a certain value the characteristic radiation from the substrate will disappear although a certain amount of scattered radiation will still be detected. The measurement of a coating thickness by X-ray absorption is not applicable if an intermediate coating is present because of the indeterminate absorption effect of the intermediate layer. The typical relationship between a coating thickness and the intensity of a characteristic emission from the substrate materials is shown in figure 2.

## 2.7 Thickness measurement by measurement of ratio of intensities

The techniques described in 2.5 and 2.6 may be combined to provide an alternative means of thickness measurement utilizing the ratio of intensities emitted from both the coating and the substrate.

## 2.8 Thickness measurement of undercoats

If the metal coating system is comprised of two layers, each of a different metal, it may be possible to use X-ray spectrometry to measure the thickness of each layer. The technique for such measurements is outlined in annex B.

## 3 FACTORS AFFECTING ACCURACY

### 3.1 Counting statistics

The production of X-ray quanta takes place in a completely random manner. This means that during a fixed time interval the number of quanta emitted will not always be the same. This gives rise to the statistical error which is inherent in all radiation measurements. In consequence, an estimate of the counting rate based on a short interval (for example, 15 s) may be appreciably different from an estimate based on a longer counting period, particularly if the counting rate is low. This error is independent of other sources of error such as those arising from mistakes on the part of the operator or the use of unreliable standards. To reduce the statistical error to an acceptable level, it is necessary to use a counting interval long enough to accumulate a sufficient number of counts.

**3.1.1** Quantitatively, the standard deviation ($\sigma$) of this random error will closely approximate the square root of the total count; that is, $\sigma = \sqrt{N}$. The true count will lie within $N \pm 2\sigma$ 95 % of the time. To judge the significance of the precision, it is helpful to express the standard deviation as a percentage of the count, that is, $100\sqrt{N}/N = 100/\sqrt{N}$. Thus, 100 000 would give a value that is 10 times as precise as the value obtained from 1 000 counts $[100/\sqrt{1\ 000}/(100/\sqrt{100\ 000}) = 10]$.

**3.1.2** A counting interval shall be chosen to provide a total count of at least 10 000, which corresponds to a statistical error of 1 %. The appropriate calibration curve is then used to determine the relevant error in the thickness measurement.

### 3.2 Coating thickness

The accuracy of the measurement will be affected by the thickness range being measured. In the curve shown in figure 1, the accuracy will be best in the portion of the curve from approximately 0,25 to 7,5 $\mu$m. The accuracy rapidly becomes poorer in the portion of the curve above approximately 10 $\mu$m. The situation is similar for the absorption curve shown in figure 2. At coating thicknesses greater than approximately 10 $\mu$m, the intensity changes very little with the coating thickness, and therefore the accuracy in that region is poor. These limiting thicknesses are, in general, different for each coating material.

### 3.3 Size of measuring area

To obtain satisfactory counting statistics (see 3.1) in a reasonably short counting period, the mask aperture shall be chosen to provide the largest possible measuring area consistent with the size and shape of the specimen. In no case shall the aperture be so large that it cannot be completely filled by a representative area of the coated surface. Caution shall also be exercised to see that use of a large aperture in conjunction with high voltage, current, or both, does not result in a signal so large as to exceed the counting rate capacity of the radiation detector being used (see 3.1).

### 3.4 Coating composition

Thickness determinations by X-ray methods may be affected by the presence of foreign materials such as inclusions, co-deposited material, and alloying metals and by voids and porosity. The sources of error will be eliminated by the use of calibration standards obtained in the same conditions as those used in the production of the coatings to be measured. If pores or voids are present, X-ray methods will give an indication of the mass of coating per unit area but not of thickness.

### 3.5 Density

If the density of the coating materials differs from that of the calibration standards, there will be a corresponding error in the thickness measurement. This is a consequence of the fact that variations in density result from variations in composition (see 3.4).

### 3.6 Substrate composition

The effect of differences in substrate composition will be relatively minor on thickness measurements made by the X-ray emission method if an intensity ratio is used (see annex A) and if the X-rays emitted by the substrate are not hard enough to excite the radiation being measured. However, when thickness measurements are made by the X-ray absorption method, the substrate composition of the test specimens has to be the same as that of the standards.

### 3.7 Substrate thickness

The effect of a thin substrate will be slight on thickness measurements by X-ray emission provided that an intensity

ratio is used (see annex A), and if the X-rays emitted by the substrate are not hard enough to excite the radiation being measured. When using the emission method, the substrate shall be sufficiently thick to prevent excitation of the coating from the reverse face on double-sided specimens. Failure to ensure this condition will introduce an error which will be large for thin coatings and which will become less as the coating thickness increases. However, when thickness is to be determined by the X-ray absorption technique, the thickness of the substrate has to exceed a certain minimum or critical thickness. It shall be established experimentally that the minimum thickness requirements have been met for a particular substrate-source combination, although it is sometimes possible to back-up the test specimen substrates with a sufficient thickness of material of identical composition. The X-ray absorption method cannot be used when one or more intermediate coating layers are present.

### 3.8 Surface cleanliness

Foreign materials such as dirt, grease, or corrosion products will lead to inaccurate thickness determinations. Protective coatings such as lacquer or chromate conversion coatings over the coating to be measured will also affect the results.

### 3.9 Specimen curvature

Thickness measurements shall be made on flat surfaces, if at all possible. In those cases where the measurement of thickness on curved surfaces cannot be avoided, a mask designed to minimize the effects of curvature shall be used. Calibration standards having the same radius of curvature as that of the test specimens could also be used to eliminate curvature effects.

### 3.10 Excitation energy

The intensity of the characteristic secondary radiation from either the coating or the substrate is strongly affected by any variation in the excitation energy, that is, by changes in voltage applied to the X-ray tube, changes in the tube current, or both. In general, the radiation intensity (quanta per unit time) is a linear function of tube current, but varies with the square of the applied voltage. Therefore, in any method based on a simple relationship between intensity and thickness, the final adjustment of excitation energy shall be made with reference to the observed intensity from a standard sample which was used to construct the working curve. However, if the method is based on intensity ratios rather than absolute intensities, minor variations in excitation energy are compensated for (see annex A).

### 3.11 Detector

Errors can be introduced by an erratic operation of the detector system, which is taken to include the associated scaling circuitry as well as the detector tube itself. If instability is suspected, a series of ten or more measurements shall be made on the same specimen, after which the standard deviation of the series shall be calculated. This result should not be significantly greater than the square root of one measurement, $\sqrt{N}$. Some forms

of instability become evident if the same specimen is measured periodically.

It should also be recognized that all radiation detection systems have an upper limit with respect to reliable counting-rate capability. Above this limit, a certain proportion of the total X-ray pulses will enter the detector during its recovery period or "dead time" and will not be counted. As a result, a measure of the true intensity will not be obtained. With large apertures in combination with high tube currents, very high counting rates may be obtained with strong element emissions such as Ni K$\alpha$. The manufacturer's instructions usually provide a procedure for determining the linear count-rate capability of a particular detection system.

### 3.12 Radiation path

To measure the radiation emitted by elements with atomic number below 24, in order to achieve higher counting rates a vacuum or helium spectrometer shall be used.

### 3.13 Conversion of counting rate to thickness

Extrapolation beyond the thickness range established by calibration standards can result in serious errors.

## 4 CALIBRATION

### 4.1 General

In taking instrument readings for the purpose of establishing an instrument calibration, exactly the same instrumental conditions, including aperture size, voltage current and measuring time, shall be used as those which will be used on test specimens.

### 4.2 Standards

Reliable standards shall be used in the calibration of any type of X-ray equipment if accurate results are to be obtained. It should be understood that prolonged counting periods will not compensate for unreliable standards. Standards representing various thickness ranges of a number of coatings on different substrates are generally available from thickness gauge manufacturers. Those that are certified for thickness (as opposed to mass per unit area) would be reliable provided that they are used for coatings of the same density and composition.

**4.2.1** The instrument shall be calibrated with thickness standards having the same coating and substrate materials as those being measured.

**4.2.2** The coating of the calibration standards shall have the same X-ray emission (or absorption) properties as the coating being measured. In the case of electroplated coatings, if the coating of the standard is electrodeposited from the same bath and under the same conditions as the coating to be measured, the X-ray properties may be assumed to be the same. For example, if the coating on the standard is gold, but not electroplated under conditions

known to be the same as the coating being measured, the X-ray properties may be assumed to be the same for the mass per unit area measurements. Under such circumstances, thickness measurements shall be corrected for density differences, unless density differences can be shown to be insignificant.

**4.2.3** If the thickness is to be determined by the X-ray absorption technique, the substrate of the thickness standards shall have the same X-ray emission properties as those of the test specimen. This shall be verified by comparing the intensities of the selected characteristic radiations of both uncoated substrate materials.

**4.2.4** In the X-ray absorption technique, the substrate thickness of the test specimen and the calibration standards shall be the same unless the critical thickness, as defined in 3.7, is exceeded.

**4.2.5** If the curvature of the coating to be measured is such as to preclude calibration of a flat surface, the curvature of the standard and that of the test specimen shall be the same.

# 5 PROCEDURES

## 5.1 Instrument operation and calibration

Operate each instrument in accordance with the manufacturer's instructions, paying attention to the factors listed in clause 3. Calibrate it in accordance with clause 4.

## 5.2 Calibration checks

Check the calibration each time the instrument is put into service, in accordance with 4.1. Measure one control specimen at frequent intervals (every 30 min) to check for drift or other changes in the equipment.

## 5.3 Precautions

Observe the following precautions :

### 5.3.1 *Substrate thickness*

If the X-ray absorption technique is used, verify that the substrate thickness of the test specimens exceeds the

critical thickness. If not, make sure that the calibration has been made with a substrate having the same thickness and emission properties as the test specimens.

### 5.3.2 *Measuring aperture*

The size of the mask aperture will depend on the size and shape of the test specimen. In no case shall the measuring aperture be larger than the coated area available on the test specimen. The test specimen shall be seated firmly and securely over the measuring opening.

### 5.3.3 *Curvature*

Use the proper measuring aperture to minimize the effects of curvature.

### 5.3.4 *Substrate material*

The secondary emission from the substrate of the standard shall be the same as that produced by the test specimen if the absorption technique is being used. Verify this by actual tests. In case of a significant difference, use new standards that agree with the test specimen.

### 5.3.5 *Surface cleanliness*

Remove all foreign materials, such as dirt, grease, lacquer, oxides, and conversion coatings from the surface, prior to the measurement, by cleaning without removing any of the coating material. Avoid specimen areas having visible defects, such as flux, acid spots, and dross, in making measurements.

### 5.3.6 *Measuring time*

Use a sufficient measuring time to obtain a repeatability that will yield the desired accuracy (see 3.1).

## 5.4 Expression of results

Convert the intensity readings to thickness units by the use of a calibration curve as described in annex A.

# 6 ACCURACY

The instrument, its calibration and its operation, shall be such that the coating thickness can be determined to within 10 % of its true value.

## ANNEX A

## CALIBRATION CURVES

If no direct reading equipment is available, it is necessary to make use of calibration curves relating either intensities or intensity ratios to corresponding thickness for each coating-substrate combination.

### A.1 EMISSION

A typical calibration curve for determining a nickel coating thickness by X-ray emission is shown in figure 1. The intensities are background-corrected; that is, the intensity at the goniometer setting for Ni Kα is obtained from a sample of the unplated brass substrate and subsequently subtracted from each of the intensity readings obtained from electroplated samples. It is apparent that, although the relationship between intensity and thickness constantly changes, it should be possible to obtain accurate nickel thickness values up to approximately 7,5 μm. A calibration curve based on intensity ratios has a very similar shape.

The form of an intensity ratio (I.R.) suitable for the measurement of thickness by X-ray emission is as follows :

$$I.R. = (I - I_0)/(I_\infty - I_0)$$

where

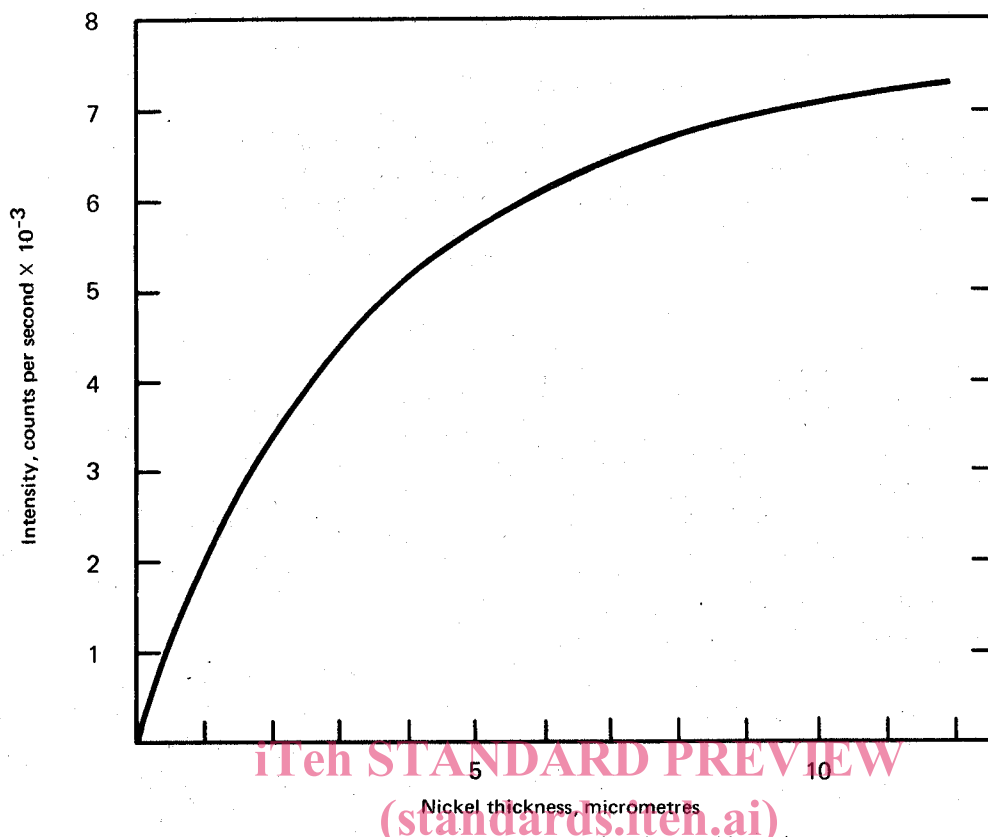$I$ is the intensity of a characteristic emission from the coating metal, for example Ni Kα;

$I_0$ is the intensity from a sample of the bare substrate at the same goniometer setting;

$I_\infty$ is the intensity from a sample of the coating metal greater than the "infinite" thickness at the same goniometer setting.

A graph of $\log(I - I.R.)$ or $\log(I_\infty - I)$ versus thickness closely approximates a straight line. Where a large number of repetitive measurements are to be made with the same aperture on samples having the same coating and substrate materials, time will be saved by using only the intensity reading of the emission from the coating without computing an intensity ratio or even making background corrections. This also avoids the possibility of additive errors which exist when three intensity readings are combined. However, when a variety of samples representing a number of different coating-substrate combinations are to be measured, the use of the intensity ratio system presents certain advantages. Among these are the fact that the same calibration curve will be valid for different aperture shapes and sizes and the effects of gradual drifting of excitation energy or detection efficiency will be compensated for.
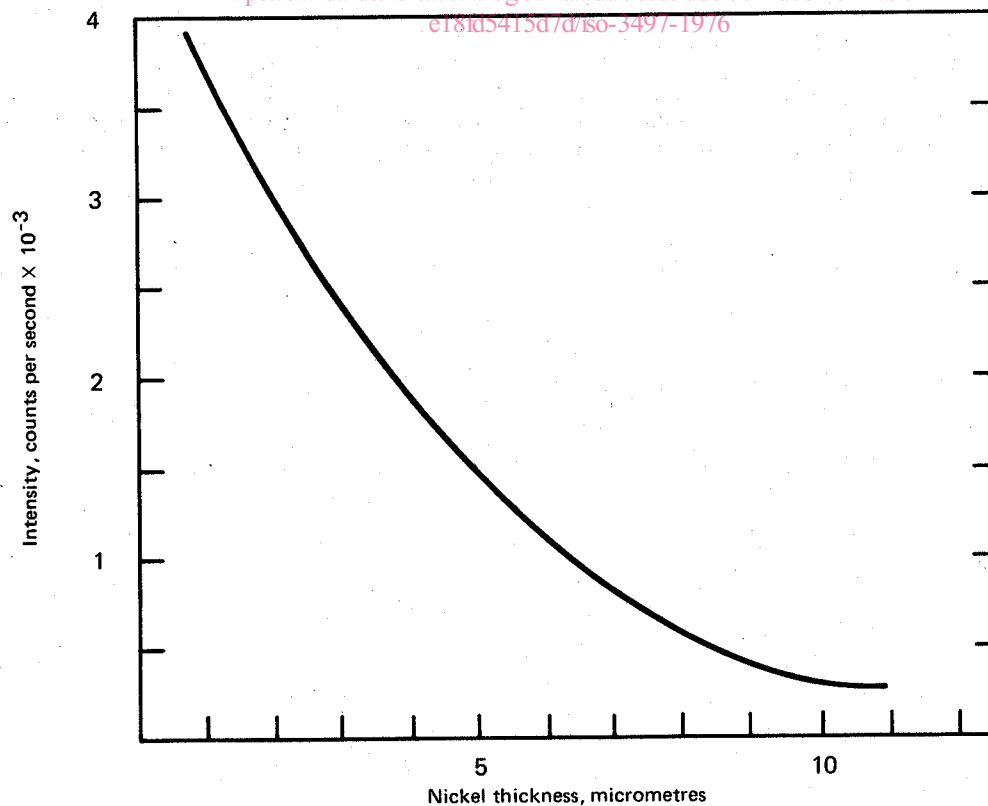
### A.2 ABSORPTION

A representative calibration curve for determining a nickel coating thickness by X-ray absorption is shown in figure 2. Here, again the intensities are background-corrected as they were in the emission technique. However, because the emission now being measured comes from the substrate, $I_0$ will correspond to a specimen of the solid, or infinitely thick coating, and $I_\infty$ to a sample of the bare substrate. The advantage of the intensity ratio curve is the same as that for the emission technique and a graph of $\log(I - I_0)$ versus thickness closely approximates a straight line. In general, the absorption technique is considered to give somewhat more accurate results, although it cannot be used when more than one coating layer is present, because of the indeterminate absorption effects of the intermediate layer(s).

FIGURE 1 — **Calibration curve for the determination of a nickel thickness by X-ray emission**

*Intensity, counts per second × 10⁻³* (y-axis)

*Nickel thickness, micrometres* (x-axis)

NOTE — Intensity is that of the Ni Kα line after subtraction of background intensity.

*Intensity, counts per second × 10⁻³* (y-axis)

*Nickel thickness, micrometres* (x-axis)

NOTE — Intensity is that of the Cu Kα line from the brass substrate after subtraction of background intensity.

FIGURE 2 — **Calibration curve for the determination of a nickel thickness by X-ray absorption**

## ANNEX B

## DOUBLE-LAYER COATINGS

**B.1** The top layer may be measured by X-ray emission (see 2.5). This measurement will be independent of the thickness of the undercoat unless the characteristic radiation of the undercoat metal is sufficiently energetic to excite the radiation being measured, for example copper or nickel under chromium. In such cases, the calibration standards should have about the same thickness of undercoat as the specimen being measured. The measurement is not sensitive to small variations in the thickness of the undercoat.

**B.2** The top layer is generally not measured by X-ray absorption because the measurement would be affected by small variations in the undercoat thickness. If the undercoat is thick enough to meet the requirements of 3.7 for the substrate, it may be used.

**B.3** The thickness of the undercoat may be determined by either the emission or the absorption method, but the measurement shall be corrected for the absorption by the top layer. The correction can be estimated from an experimentally determined curve after the thickness of the top layer is measured.