SLOVENSKI STANDARD
SIST EN 10318:2005

01-september-2005

Ugotavljanje debeline in kemiļ ne sestave kovinskih prevlek na osnovi cinka in aluminija ï Rutinska metoda

Determination of thickness and chemical composition of zinc- and aluminium-based metallic coatings - Routine method

Bestimmung der Dicke und der chemischen Zusammensetzung metallischer Überzüge auf Basis von Zink und Aluminium - Standard-Verfahren

Détermination de l'épaisseur et de la composition chimique des revetements en zinc et en alliage d'aluminium - Méthode de routine

Ta slovenski standard je istoveten z: **EN 10318:2005**

ICS:

17.040.20	Lastnosti površin	Properties of surfaces
25.220.40	Kovinske prevleke	Metallic coatings

SIST EN 10318:2005 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 10318

May 2005

ICS 17.040.20; 25.220.40

English version

Determination of thickness and chemical composition of zinc- and aluminium-based metallic coatings - Routine method

Détermination de l´épaisseur et de la composition chimique des revêtements en zinc et en alliage d´aluminium - Méthode de routine

Bestimmung der Dicke und der chemischen Zusammensetzung metallischer Überzüge auf Basis von Zink und Aluminium - Standard-Verfahren

This European Standard was approved by CEN on 21 March 2005.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Contents

Foreword

This European Standard (EN 10318:2005) has been prepared by Technical Committee ECISS/TC 20 “Methods of chemical analysis of ferrous products”, the secretariat of which is held by SIS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

1 Scope

This European Standard specifies a glow discharge optical emission spectrometric method for the determination of the thickness and chemical composition of metallic surface coatings consisting of zinc and aluminium based alloys. The alloying elements considered are aluminium, nickel, silicon and lead.

This method is applicable to zinc contents between 40 % (*m/m*) and 100 % (*m/m*); aluminium contents between 0,01 % (*m/m*) and 60 % (*m/m*); nickel contents between 0,01 % (*m/m*) and 15 % (*m/m*); silicon contents between 0,01 % (*m/m*) and 3 % (*m/m*); lead contents between 0,005 % (*m/m*) and 0,1 % (*m/m*).

2 Normative references

Not applicable.

3 Principle

The analytical method described here involves the following processes:

a) Cathodic sputtering of the surface coating in a direct current glow discharge device;

b) Optical excitation of the analyte atoms in the plasma formed in the glow discharge device;

c) Spectrometric measurement of characteristic emission spectral lines of the analyte atoms as a function of sputtering time (depth profile); and

d) Conversion of the depth profile in units of intensity versus time to mass fraction versus depth by means of calibration functions (quantification). Calibration of the system is achieved by measurements on calibration samples of known chemical composition and measured sputtering rate.

4 Apparatus

4.1 Glow discharge optical emission spectrometer

4.1.1 General

An optical emission spectrometer equipped with a Grimm type (1) or similar direct current glow discharge source and a simultaneous optical spectrometer, incorporating suitable spectral lines for the analyte elements (see Table 1 for recommended lines) shall be used.

The inner diameter of the hollow anode of the glow discharge shall be in the range 2 mm to 8 mm. A cooling device for thin samples, such as a metal block with circulating cooling liquid, is also recommended, but not strictly necessary for implementation of the method.

It is desirable for the instrument to conform to the performance specifications given in 4.1.2 and 4.1.3, to be evaluated in 6.2.6.

4.1.2 Minimum repeatability

Perform 10 measurements of the emission intensity on a homogeneous bulk sample with a content of the analyte exceeding 1 % (*m/m*). Allow the discharge at least 60 s stabilisation time (often referred to as *preburn*) before each intensity measurement. Each measurement shall be located on a newly prepared surface of the sample. Calculate the standard deviation of the 10 measurements. The standard deviation should not exceed 2 % of the mean intensity of the analyte. If this is the case, repeat the test two more times. If the high standard deviation is repeatable, there is probably some malfunction in the instrument or the sample used is not homogeneous. Before proceeding, the cause of the problem should be investigated and rectified.

4.1.3 Limit of detection

Detection limits are instrument-dependent and matrix-dependent. Consequently, the detection limit for a given analyte cannot be uniquely determined for every available instrument or for the full range of Zn-based alloys considered here. For the purposes of this document, the detection limit for each analyte will be acceptable if it is equal to or less than one third of the lowest concentration to be determined in the intended applications. The detection limit is determined using the method explained below.

a). Select a bulk sample to be used as a blank. The sample composition should be similar to the coatings to be analyzed in terms of the elemental composition of the matrix. Further, it shall be known to contain less than 0,1 mg kg^{-1} of the analyte.

b). Perform ten replicate burns on the blank. For each burn, acquire the emission intensity at the analytical wavelength for 10 s. These are the background emission intensity measurements. The glow discharge conditions used should be the same as those that will be used in the analysis of the coated samples. For each measurement, the blank should be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. An unsputtered area of the surface of the blank for each individual burn shall be used.

c). Compute the detection limit using the following equation:

$$DL = \frac{3\times S}{m}$$

where

DL is the detection limit;

S is the standard deviation of the ten background intensity measurements performed in step (2);

m is the analytical sensitivity derived from the instrument calibration expressed as the ratio of intensity to mass fraction.

If the detection limit calculated is greater than one third of the lowest concentration to be determined in the intended applications, then the test should be repeated. If the second value calculated is also greater than one third of the lowest concentration to be determined in the intended applications, then there may be an instrument malfunction. In such a case, the problem should be investigated prior to analyzing unknown samples.

4.2 Data acquisition

Since the principle of determination is based on continuous sputtering of the surface coating, the spectrometer shall be equipped with a digital readout system for time-resolved measurement of the emission intensities. A system with capability for data acquisition speed of at least 500 measurements/second per spectral channel is recommended, but for the applications within the scope of this standard a speed of 2 measurements/second per spectral channel may be acceptable.

5 Sampling

Carry out sampling in accordance with the recommendations of the manufacturer of the coated material. In general, the edges of a coated strip should be avoided. The size of the test samples should be suitable for the glow discharge source used. Typically, round or rectangular samples with a width of 20 mm to 100 mm are suitable.

6 Procedure

6.1 Selection of spectral lines

For each analyte to be determined there exists a number of spectral lines which can be used. Suitable lines shall be selected on the basis of several factors including the spectral range of the spectrometer used, analyte concentration range, sensitivity of the spectral lines and spectral interference from other elements present in the samples. In this type of application, where most of the analytes of interest are major elements in the samples, special attention shall be paid to the occurrence of self-absorption of certain highly sensitive spectral lines. Self-absorption may cause severe non-linearity of calibration curves at high analyte concentration levels, and such lines should therefore be avoided for the determination of majors. In Table 1, some suggestions concerning suitable spectral lines are given.

Table 1 — Suggested spectral lines for determination of given elements

Element	**Wavelength** (nm)	**Estimated useful concentration range** % (m/m)	**Comments**
Zn	330,26	0,001 to 100	
Zn	334,50	0,001 to 100	
Zn	481,053	0,001 to 100	
Al	172,50	0,1 to 100	
Al	396,15	0,001 to 100 [a]	Self-absorption
Ni	231,603	0,01 to 100	
Ni	341,78	0,001 to 100 [a]	Weak self-absorption
Ni	349,30	0,005 to 100 [a]	Weak self-absorption
Pb	202,20	0,001 to 10	
Pb	405,87	0,01 to 100	
Si	212,41	No data available	
Si	251,61	No data available	
Si	288,16	0,001 to 20	
Fe	249,318	0,01 to 100	
Fe	259,94	0,01 to 100	
Fe	271,44	0,1 to 100	
Fe	371,94	0,005 to 100 [a]	Weak self-absorption
Fe	379,50	0,01 to 100	
Cu	296,12	0,01 to 100	
Cu	327,40	0,001 to 5 [a]	Strong self-absorption

[a] Use of non-linear calibration curve recommended.

6.2 Optimising the glow discharge spectrometer settings

6.2.1 General

Follow the manufacturer's instructions for preparing the instrument for use. In particular, check that the entrance slit to the spectrometer is correctly adjusted, following the procedure given by the instrument manufacturer. This ensures that the emission intensities are measured on the peaks of the spectral lines for optimal signal to background ratio. For further information, see e.g. ISO 14707.

The source parameters shall be chosen to achieve three aims: adequate sputtering of the sample, to reduce the analysis time without over-heating the coatings; good crater shape, for good depth resolution; and constant excitation conditions in calibration and analysis, for optimum accuracy. There are often tradeoffs among the three specified aims.

Modern DC glow discharge spectrometers usually have provisions for complete control/measurement of the electrical parameters (current, voltage, power), allowing any two of these parameters to be locked to constant values by varying the pressure (active pressure regulation). Older spectrometers often lack an active pressure regulation system, but the pressure can still be adjusted manually to maintain nearly constant current and voltage during calibration measurements.

6.2.2 Constant applied current and voltage

The two control parameters are applied current and voltage. Set the power supply for the glow discharge source to constant current – constant voltage operation. First set the current and voltage to typical values recommended by the manufacturer. If no recommended values are available, set the current to a value in the range 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode, 40 mA to 100 mA for a 7 mm or 8 mm anode. If no beforehand knowledge about the optimum current is at hand, it is recommended to start with a value somewhere in the middle of the recommended range, and the voltage at 700 V.

Set the high voltage of the detectors as described in 6.2.4.

Adjust the discharge parameters as described in 6.2.5, adjusting first the current and if necessary the voltage.

6.2.3 Constant applied current and pressure

The two control parameters are applied current and pressure. Set the power supply for the glow discharge source to constant current operation. First set the current to a typical value recommended by the manufacturer. If no recommended values are available, set the current to a value in the range 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode, 40 mA to 100 mA for a 7 mm or 8 mm anode. If no beforehand knowledge about the optimum current is at hand, it is recommended to start with a value somewhere in the middle of the recommended range. Sputter a typical coated test sample, and adjust the pressure until a voltage of approximately 600 V is attained in the coating.

Set the high voltage of the detectors as described in 6.2.4.

Adjust the discharge parameters as described in 6.2.5, adjusting first the current and if necessary the pressure.

Before sputtering a new sample type, make a test run in order to ensure that the voltage is not altered more than 5 % from the previously selected value. If this is the case, readjust the pressure until the correct value is attained. These conditions are then used during analysis.

6.2.4 Setting the high voltage of the detectors

Select test samples with coatings of all types to be determined. Using these samples, run the source while observing the output signals from the detectors for the analyte atoms. Adjust the high voltage of the detectors in such a way that sufficient sensitivity at the lowest analyte concentrations is ensured, without saturation of the detector system at the highest analyte concentrations.

6.2.5 Adjusting the discharge parameters

For each type of test sample carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the coating completely and continue well into the base material. By observing the emission intensities as a function of sputtering time (often referred to as the qualitative depth profile), verify that the selected source settings give stable emission signals throughout the depth profile and into the substrate. Unstable emission signals may indicate thermal instability on the sample surface; sample cooling is beneficial in this regard. If this is found not to be the case, reduce one of the control parameters by a small amount and sputter through the coatings again. If the stability is still unsatisfactory, reduce the other control parameter by a small amount and repeat the measurements. If found necessary, repeat this procedure for a number of control parameter combinations until stable emission conditions are obtained.

6.2.6 Preliminary precision test

Select a few suitable bulk calibration samples (see 6.3.3), and perform tests described in 4.1.2 and 4.1.3. Ensure that the discharge parameters and detector high voltages are the same as those selected for the coated materials. These tests are carried out to confirm that the operation procedure is adequate.

6.3 Calibration

6.3.1 General

Calibration of the system consists of determining, for each analyte and spectral line, a quantity known as the *emission yield* (2,3,4), which is defined as the integrated emission intensity per unit mass of the analyte. The principle of quantification used in this standard is based on the observation that the emission yield is a matrix-independent quantity, or at least very nearly so (3,5). In order to determine the emission yield, it is necessary to know both the chemical composition and the sputtering rates (mass loss rate) of the calibration samples.

It is not necessary to prepare a new calibration for each series of determinations of unknown samples. Instead, only a limited number of the calibration samples are re-run in order to determine the instrumental drift in sensitivity and background for each spectral channel used in the method. For each channel, a high and a low intensity point is required. The measured intensities are then corrected for the drift prior to the calculation of the quantitative results. This procedure, referred to as *drift correction or recalibration*, is routinely employed in both optical emission and X-ray fluorescence spectrometry for bulk analysis.

6.3.2 Calibration samples

6.3.2.1 General

Whenever possible, spectrometric calibration samples issued as CRMs (Certified Reference Materials) should be used. Due to the quantification being based on emission yields, the calibration samples need not be very similar to the coating materials in composition, but shall have sputtering rates which are reproducible. In particular, pure or nearly pure zinc samples are not recommended due to difficulties in obtaining reproducible and stable sputtering rates in zinc. Furthermore, high purity metals are not necessary in order to calibrate correctly for high concentrations, but they are valuable for the determination of the spectral backgrounds. The following considerations are the most important in the selection of the calibration samples:

a) there shall be at least 5 calibration samples for each analyte, covering a range from zero to the highest concentrations to be determined;

b) samples shall be homogeneous;

c) samples shall have well determined sputtering rates.

Based on these general recommendations, the following types of calibration samples are suggested in 6.3.2.2 to 6.3.2.7. It should be noted that these recommendations constitute a minimum requirement, and additional calibration samples of other alloy types containing the analytes may be used.

6.3.2.2 Brass calibration samples

Select at least two brass samples with zinc contents of 25 % to 50 % (*m/m*); aluminium contents of 1 % to 4 % (*m/m*); lead contents of 1 % to 4 % (*m/m*).

6.3.2.3 ZnAl alloy samples

Select at least two ZnAl alloy samples with a zinc content of 40 % to 95 % (*m/m*).

6.3.2.4 Stainless steel samples

Select at least two stainless steels with nickel contents of 10 % to 40 % (*m/m*).

6.3.2.5 Nickel based alloy samples

Select at least one nickel based alloy sample with a nickel content of more than 70 % (*m/m*).

6.3.2.6 Aluminium - silicon alloy samples

Select at least one aluminium-silicon alloy sample with a silicon content of 5 % to 10 % (*m/m*).

6.3.2.7 High purity copper sample

Select a high purity copper sample with concentrations of the analytes less than 0,001 % (*m/m*). This sample can be used as zero points for all analytes except copper, even if the exact concentrations of the analytes are not known.

6.3.3 Determination of the sputtering rate of calibration samples

The term *sputtering rate* is understood here to be equivalent to the mass loss rate during sputtering in the glow discharge. In order to determine this quantity for the calibration samples, the following procedure is recommended:

a) prepare the sample surface according to recommendations from the instrument manufacturer;

b) adjust the glow discharge current and voltage to those selected in 6.2;

c) sputter the sample for a time estimated to result in a crater 20 µm to 40 µm deep, recording the total sputtering time;

d) repeat c) several times if the sample surface area is sufficiently large, recording the total sputtering time for each crater;

e) measure the average depth of each crater by means of an optical or mechanical profilometer device, performing at least 4 profile traces in different directions across the centre of the crater;

f) calculate the sputtered volume of each crater, the sputtered mass as the volume multiplied by the density of the sample;

g) calculate the sputtering rate for each crater as the mass loss divided by the total sputtering time;

h) calculate the average sputtering rate and the standard deviation from the measurements of each crater.

The profilometer should have an accuracy in the depth calibration better than 5 %.

NOTE The sputtered mass can also be determined by weighing samples before and after sputtering. However, this requires the use of scales of extremely high accuracy, and the uncertainty in such measurements is generally greater than those obtained by crater depth measurements.

6.3.4 Emission intensity measurements of calibration samples

The procedure for measuring the calibration samples is as follows:

a) prepare the surfaces of the calibration samples according to the instrument manufacturer's instructions.

b) adjust the instrument to the current and voltage settings selected in 6.2, a preburn time of 100 s to 200 s and a signal integration time of 5 s to 30 s.