BRITISH STANDARD

BS EN 10318:2005

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

The European Standard EN 10318:2005 has the status of a British Standard

ICS 17.040.20; 25.220.40

Confirmed
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British Standards

National foreword

This British Standard is the official English language version of EN 10318:2005.

The UK participation in its preparation was entrusted to Technical Committee ISE/18, Sampling and analysis of Iron and Steel, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
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EN 10318

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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.

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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.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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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of an identical text or by endorsement, at the latest by November 2005, and conflicting national standards shall be withdrawn at the latest by November 2005.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.

c) measure the emission intensities of the analytes zinc, aluminium, nickel, iron, silicon, copper and lead for each calibration sample. Additional analytes, which are present in the calibration samples, may be measured simultaneously. The units in which the intensities are given is of no importance, commonly used units are counts per second (cps) or volts (V). Measure each sample at least two times and calculate the average values.

6.3.5 Calculation of calibration constants

Calculation of calibration constants constitutes plotting data from the calibration measurements in appropriate graphs and fitting to a curve by so-called regression calculation. Follow one of the procedures given in Annex A (normative) appropriate for the instrument and software system available.

7 Verification of the analytical accuracy

Select from the set of calibration samples a few samples which contain the relevant analytes in concentrations as close as possible to those found in the coating types to be determined. Prepare the sample surfaces in the same way as for calibration measurements. Adjust the operating conditions for each sample to the same values as those used during calibration. Run each sample as an unknown for a time resulting in a sputtered depth of 20 µm to 40 µm. Calculate the composition and sputtered depth using the calibration constants of the method.

Verify that the measured fraction of each analyte is accurate to within the acceptable uncertainty relative to the certified value. The acceptable uncertainty cannot be uniquely defined for all analytes, but for majors, a relative accuracy better than 5 % is achievable in most cases. Verify also that the measured sputtered depth is accurate to within 10 % of that calculated from the known sputtering rate of the sample.

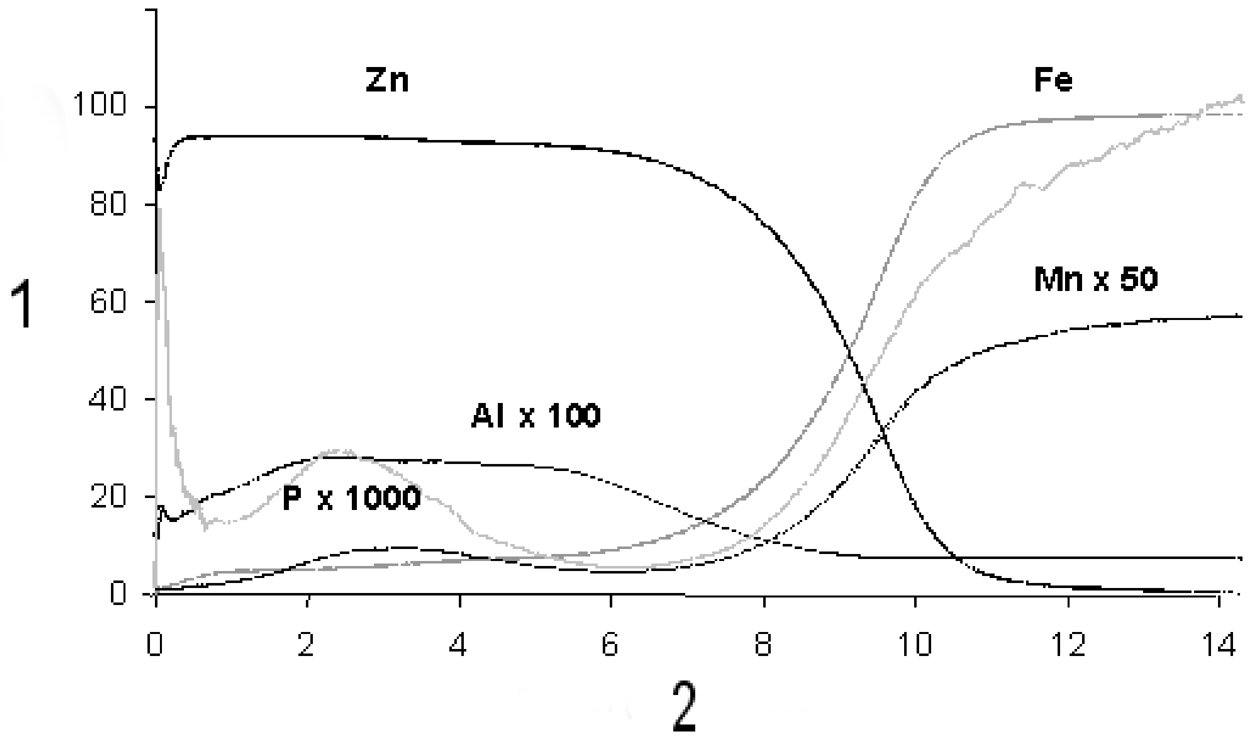
If coated test samples with well determined composition and coating thickness are available, run these samples as unknowns and verify that measured composition and thickness are accurate within the acceptable uncertainty.

If unacceptably large deviations between measured and certified values are found, the instrument shall be drift corrected as described in 6.3. The verification tests shall then be repeated. If the deviations are still unacceptably large, the calibration shall be checked and possibly repeated.

8 Expression of results

8.1 Method of calculation

All analytical information obtained is contained in the quantitative depth profile (Figure 1).



Key

1 Analyte weight in percent

2 Depth in micrometers

Figure 1 — Quantitative depth profile of a Galvanneal (ZnFe) coating on steel

In order to determine the total coating weights per element, the area under each curve is integrated for the total depth of the coating. For the major elements, the following recommendation for determination of the integration depth is given:

a) determine coating thickness as the depth where the concentration of the major element is reduced to 50 % of the average value in the coating;

b) determine the width of the interface region (= the practical depth resolution) as the difference between the two points in depth where the concentrations of the major element are 84 % and 15 % respectively of the average value in the coating;

c) determine the integration depth as the sum of the coating thickness and the interface width.

The average concentrations of each element are determined as the fractions of the sum of the coating weights of all elements present in the coating.

8.2 Precision

A planned trial of this method was carried out by eight laboratories, using six industrially produced coated steels as test materials. Each laboratory made three determinations on one side of each material, calculating the integrated coating weight of each element. The elements determined in the coatings were Zn, Al, Ni, Pb and Si. In order to obtain data relevant to the limits of determination, Al, Ni, Pb and Si were also determined in the materials where these elements are not present at all or at very low trace levels.

The test materials are listed in Table 2.

Table 2 — Test materials used

Identity	**Type**	**Approximate total coating weight** (g/m^2)	**Approximate composition** % (*m/m*)
HD 1	Hot dipped galvanised steel sheet	60	Al 0,6 Pb 0,001
HD 2	Hot dipped galvanised steel sheet	130	Al 0,3 Pb 0,08
ZnNi	Electroplated ZnNi alloy on steel sheet	45	Ni 12
Galvanneal	Hot dipped galvanised and annealed steel sheet	50	Al 0,3 Fe 12
Galfan	Hot dipped galvanised steel sheet	120	Al 5
Aluzinc	Hot dipped galvanised steel sheet	90	Al 53 Si 2

The total coating weight and the major element Zn are reported in units of (g/m^2); all other elements in units of % (m/m). The results were treated statistically in accordance with ISO 5725-1, ISO 5725-2 and ISO 5725-3. The test results are summarised in Tables 3 to 8.

Table 3 — Total coating weight repeatability and reproducibility

Identity	**Total coating weight** (g/m^2)	**Repeatability** r	**Reproducibility** R
HD 1	58,7	7,3	9,0
HD 2	130,2	16,2	23,9
ZnNi	48,3	5,5	9,5
Galvanneal	n.d.	n.d.	n.d.
Galfan	121,8	9,5	23,0
Aluzinc	85,3	4,4	17,0

Table 4 — Zinc coating weight repeatability and reproducibility

Identity	**Zinc coating weight** (g/m^2)	**Repeatability** r	**Reproducibility** R
HD 1	57,0	7,3	9,0
HD 2	129,7	16,2	23,9
ZnNi	43,0	5,4	8,5
Galvanneal	41,4	6,3	11,1
Galfan	115,5	9,5	23,0
Aluzinc	38,3	4,3	11,5

Table 5 — Aluminium repeatability and reproducibility

Identity	Aluminium content % (*m/m*)	Repeatability *r*	Reproducibility *R*
HD 1	0,659	0,061	0,228
HD 2	0,339	0,04	0,145
ZnNi	0,005 5	0,003 7	0,008 9
Galvanneal	0,263	0,035	0,08
Galfan	4,68	0,34	1,07
Aluzinc	52,2	1,0	3,3

Table 6 — Nickel repeatability and reproducibility

Identity	Nickel content % (*m/m*)	Repeatability *r*	Reproducibility *R*
HD 1	0,001 1	0,000 31	0,005 9
HD 2	0,002 7	0,001 1	0,003 9
ZnNi	11,30	1,06	4,25
Galvanneal	n.d.	n.d.	n.d.
Galfan	0,001 6	0,001 1	0,005 3
Aluzinc	n.d.	n.d.	n.d.

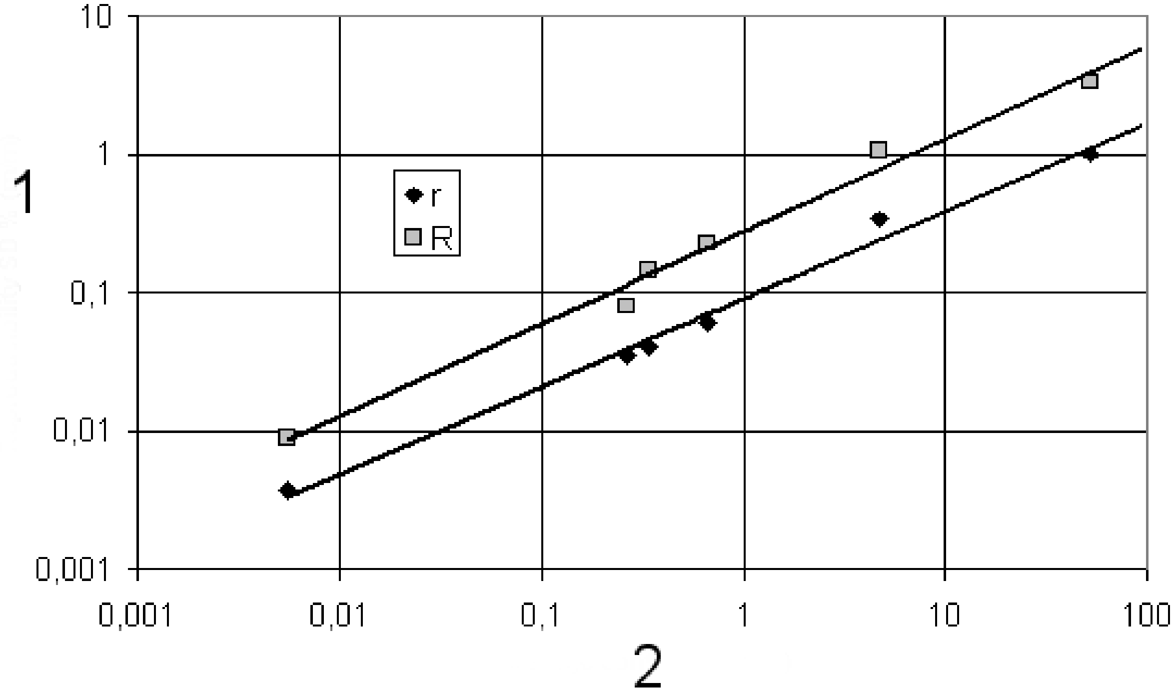
Table 7 — Lead repeatability and reproducibility

Identity	Lead content % (*m/m*)	Repeatability *r*	Reproducibility *R*
HD 1	0,000 17	0,001 1	0,003 9
HD 2	0,081	0,014	0,024
ZnNi	0,006 9	0,000 61	0,007 8
Galvanneal	0,001 8	0,006 7	0,006 7
Galfan	0,000 71	0,000 37	0,000 38
Aluzinc	n.d.	n.d.	n.d.

Table 8 — Silicon repeatability and reproducibility

Identity	Silicon content % (*m/m*)	Repeatability *r*	Reproducibility *R*
HD 1	0,001 9	0,001 0	0,003 8
HD 2	0,000 8	0,001 3	0,001 9
ZnNi	0,005 2	0,002 3	0,005 7
Galvanneal	0,001 9	0,001 0	0,004 0
Galfan	0,004 2	0,000 9	0,005 3
Aluzinc	2,02	0,032	0,77

NOTE The poor reproducibility in several cases mainly reflect the inhomogeneity of industrial materials.

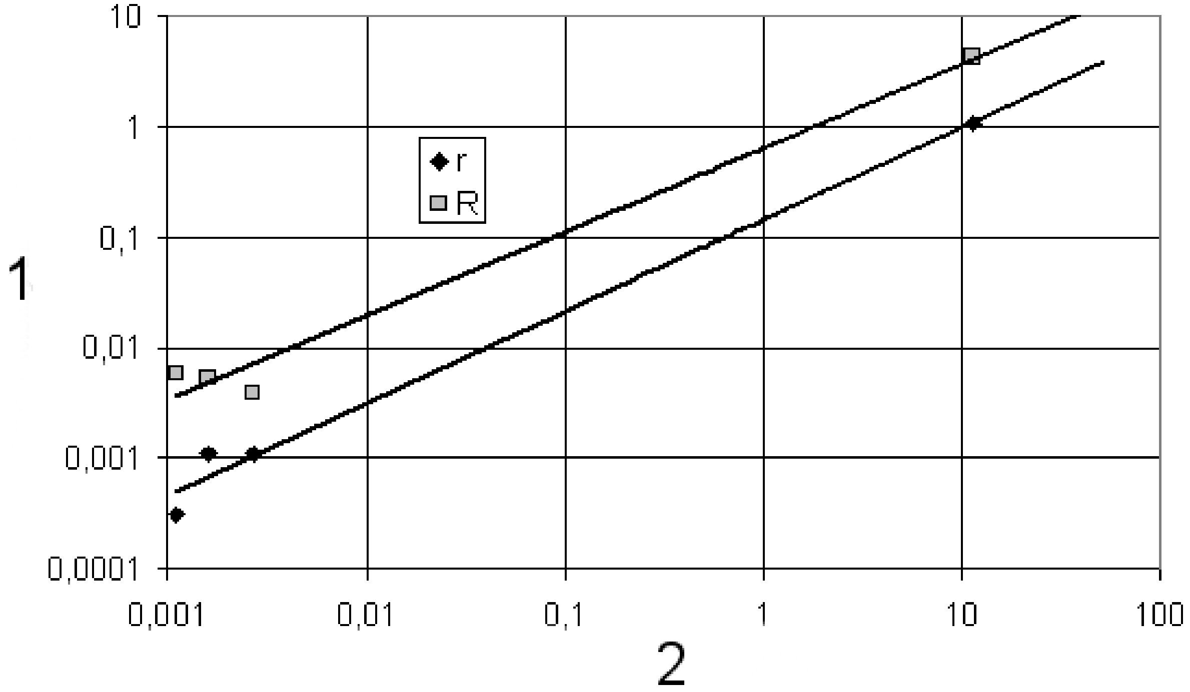


Key

1 Reproducibility SD % (*m/m*)

2 Average content % (*m/m*)

Figure 2 — Log-log diagram Aluminium

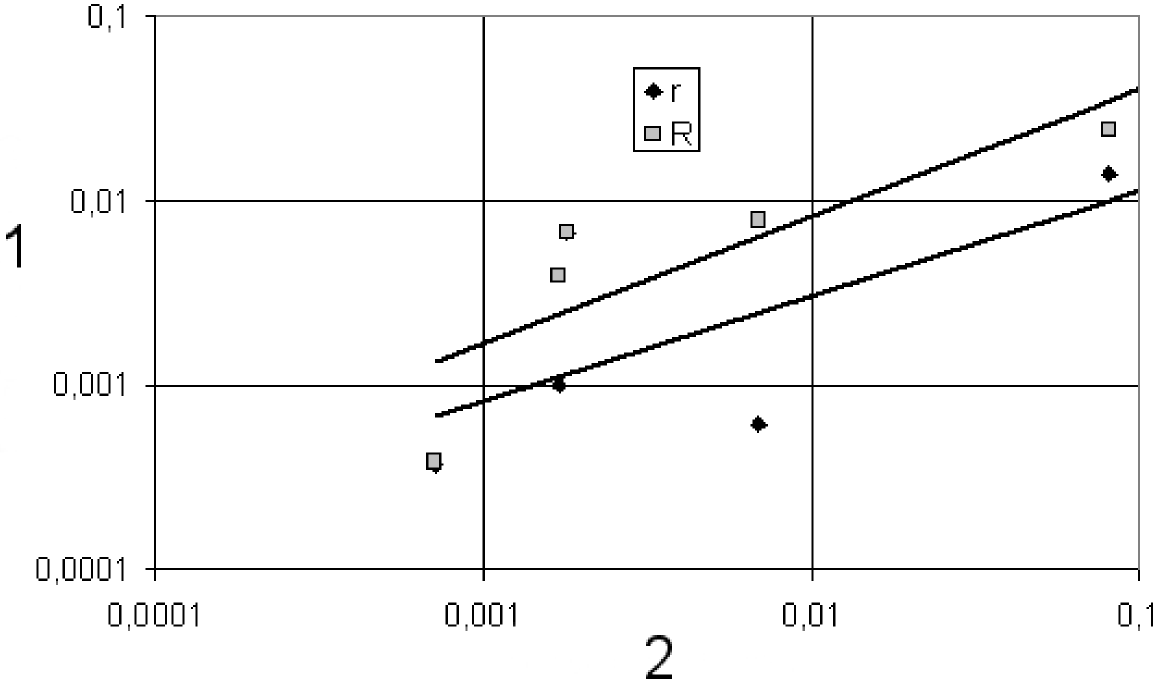


Key

1 Reproducibility SD % (*m/m*)

2 Average content % (*m/m*)

Figure 3 — Log-log diagram Nickel

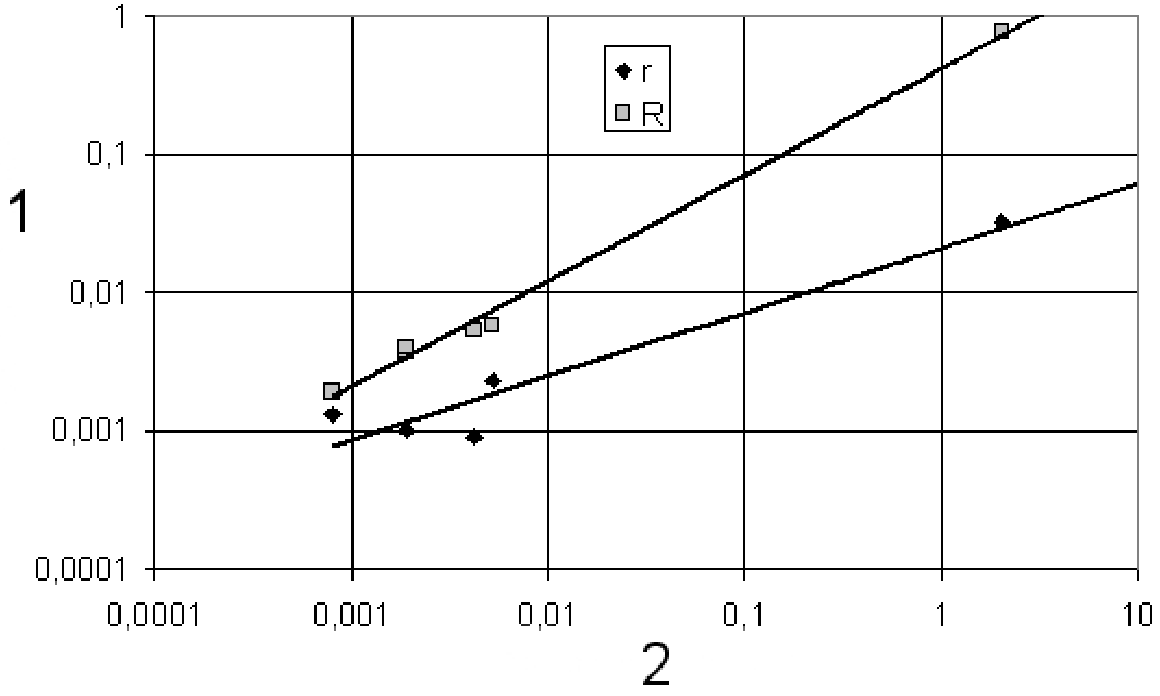


Key

1 Reproducibility SD % (*m/m*)

2 Average content % (*m/m*)

Figure 4 — Log-log diagram Lead



Key

1 Reproducibility SD % (*m/m*)

2 Average content % (*m/m*)

Figure 5 — Log-log diagram Silicon

9 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

b) method used, by reference to this document;

c) results and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this document or any optional operation which may have influenced the results.

Annex A
(normative)

Calculation of calibration constants and quantitative evaluation of depth profiles

A.1 Calculation of calibration constants

In this document, the emission yield $R_{i\lambda}$ of element i and spectral line λ is defined by the following equation:

$$R_{\mathrm{ia}} = \left[\left(l_{\mathrm{i}\lambda} - B_{\lambda} \right) \times \frac{\Delta t}{m_{\mathrm{i}}} \right] \tag{A.1}$$

where

m_{i} is the sputtered mass of element i during time increment Δt;

$I_{\mathrm{i}\lambda}$ is the emission intensity of spectral line λ of element i;

B_{λ} is the spectral background intensity at wavelength λ.

As defined here, $R_{\mathrm{i}\lambda}$ depends on atomic as well as instrument specific parameters. It is therefore necessary to determine the emission yields for each apparatus used.

The quantity m_{i} is also given by the following equation:

$$m_{\mathrm{i}} = q_{\mathrm{s}} \times c_{\mathrm{is}} \times \Delta t \tag{A.2}$$

where

q_{s} is the sputtering rate of sample s;

c_{is} is the concentration of element i in sample s.

It can be inferred from Equation (A.1) that by plotting the sputtered mass of element i as a function of the time-integrated intensity of the corresponding spectral line, the inverse of the emission yield is obtained as the slope of the calibration curve.

Combining Equations (A.1) and (A.2) gives the following alternative expression for determination of the emission yield:

$$q_{\mathrm{s}} \times c_{\mathrm{is}} = \frac{\left(l_{\mathrm{it}\lambda} - b_{\lambda} \right)}{r_{\mathrm{i}\lambda}} \tag{A.3}$$

In practical analytical work, it is recommended to use Equation (A.3) for the determination of the emission yields rather than Equation (A.1). This equation can conveniently be modified to non-linear calibration curves by incorporating a second-order term:

$$q_{\mathrm{s}} \times c_{\mathrm{is}} = \frac{l_{\mathrm{it}\lambda}}{R_{\mathrm{i}\lambda}} + \mathrm{k} \times \left(\frac{l_{\mathrm{it}\lambda}}{R_{\mathrm{i}\lambda}} \right)^{2} - \frac{B_{\lambda}}{R_{\mathrm{i}\lambda}} \qquad \text{(A.4)}$$

where

k is a constant describing the degree of non-linearity

If necessary a third order term can also be added to Equation (A.4). The actual calibration constants shall be obtained by regression analysis of the calibration data according to a least square fit algorithm.

A third form of calibration function based on the concept of constant emission yield is obtained by multiplying the measured emission intensities of each calibration standard with a sputtering rate correction factor, which normalises the intensities to that of a reference material of well determined sputtering rate. This procedure, commonly referred to as the intensity normalisation technique, gives the following expression for calibrating with respect to sample concentrations:

$$c_{\mathrm{is}} = k_{\mathrm{i}\lambda} \times c_{\mathrm{is}} = k_{\mathrm{i}\lambda} \times l_{\mathrm{i}\lambda} \times \left(\frac{q_{\mathrm{ref}}}{q_{\mathrm{s}}} \right) - B_{\lambda\mathrm{c}} \qquad \text{(A.5)}$$

where

$k_{\mathrm{i}\lambda}$ is equal to $1/(R_{\mathrm{i}\lambda} \times q_{\mathrm{ref}})$;

q_{ref} is the sputtering rate of the selected reference material;

$q_{\mathrm{ref}}/q_{\mathrm{s}}$ is the sputtering rate correction factor;

$B_{\lambda\mathrm{c}}$ is the spectral background at wavelength λ, given in concentration units (often referred to as *background equivalent concentration*).

The main reason why Equation (A.5) is often used for calibration in commercially available systems is that it has the same general form as the calibration functions conventionally used in bulk analysis, where the actual concentration is plotted as a function of emission intensity. The number q_{ref} is normally selected as the sputtering rate of some frequently used base material for calibration standards, e.g. pure iron. This has the effect that for several irons based calibration samples, the sputtering rate correction factor is close to unity. If q_{ref} is set equal to 1 (unity sputtering rate), Equation (A.5) becomes numerically equivalent to Equation (A.3).

The emission yields vary with the current, voltage and possibly the pressure [4]. It is therefore essential that these parameters are kept as closely as possible at the same levels during measurement of coated samples as during calibration. Since it is impossible in practice to maintain all three parameters constant for all samples, priority is given to maintaining current and voltage constant, utilising the pressure as a variable parameter. There exists a method to correct for voltage and current variations by means of an empirically derived function (4) and this type of correction is often implemented in software based on the intensity normalisation method according to Equation (A.5). However, such corrections for voltage and current are not to be included in this standard method. If available in the spectrometer software, the user shall therefore ensure that the voltage to current corrections are disabled in order to implement the method correctly.

NOTE 1 The spectral background terms in Equations (A.1), (A.3) and (A.5) are not true constants, they are more or less matrix-dependent as was pointed out in 4.1.3. In practical work, it is advisable always to select the lowest measured intensity as fixed the background for each spectral line.

NOTE 2 All commercially available instruments manufactured today have provisions to subtract additional background signals from other analyte elements (line interference corrections). Where applicable, such corrections should be implemented.

A.2 Calculation of concentrations and sputtered mass

The calculation of elemental concentrations and sputtered mass can proceed according to two different sets of algorithms described below, depending on which calibration function was used according to 6.3.5. The final results are, however, equivalent.

A.2.1 Calculation based on calibration for sputtered mass per element

If Equation (A.1) or (A.3) was used for calibration, the following calculation steps are to be carried out.

For each segment j and corresponding time increment Δt_j of the depth profile, calculate the sputtered mass m_{ij} of element i according to the following equation:

$$m_{ij} = \left[\left(l_{it\lambda} - B_{\lambda} \right) \times \frac{\Delta t}{R_{i\lambda}} \right] \tag{A.6}$$

If Equation (A.4) has been used, the second order term is added in a straight-forward manner.

Provided that the sum of all determined elements constitute > 98% of the analysed material, calculate the total sputtered mass, M_j of segment j of the depth profile using the equation:

$$M_j = \sum M_{ij} \tag{A.7}$$

The concentration c_{ij} of element I in segment j is given by the following equation:

$$c_{ij} = 100 \times \frac{m_{ij}}{M_j} \tag{A.8}$$

where

c_{ij} is given in units of % by mass.

The total sputtered mass, M_i, of element i in any arbitrary section of the depth profile is given by the following equation:

$$M_i = \sum_j M_{ij} \tag{A.9}$$

The analyst determines where the summation range over segment j is.

A.2.2 Calculation based on calibration for concentrations of the elements

If Equation (A.5) was used for calibration, the following calculation steps are to be carried out.

Provided that the sum of all determined elements constitute > 98% of the analysed material, the concentration c_{ij} of element i in segment j is given by the following equation:

$$cij = \frac{\left(\mathrm{k}_{i\lambda} \times l_{ij\lambda} - \mathrm{B}_{\lambda c} \right)}{\sum_i \left(\mathrm{k}_{i\lambda} \times l_{ij\lambda} - \mathrm{B}_{\lambda c} \right)} \tag{A.10}$$

where

$\mathrm{k}_{i\lambda}$, B_{λ} are the calibration constants calculated from Equation (A.5).

NOTE Equation (A.10) incorporates a sum normalisation of all concentrations to 100 %.

For each segment, j, of the depth profile, calculate the sputtering rate, q_i, using the equation:

$$q_j = q_{ref} \times \sum_i \frac{\left(K_{i\lambda} \times l_{ij\lambda} - B_{\lambda c}\right)}{100} \qquad (A.11)$$

where

q_{ref} is the sputtering rate of the selected reference material.

For each segment, j, and corresponding time increment, Δt_I, of the depth profile, the sputtered mass, m_{ij}, of the element is given by the following equation:

$$m_{ij} = q_i \times c_{ji} \times \Delta t_i \qquad (A.12)$$

The total sputtered mass, M_i of element i is calculated according to Equation (A.9) of A.2.1.

A.3 Calculation of sputtered depth

A.3.1 General

The analytical method described in this document determines the sputtered mass and concentrations of each element. In order to determine the sputtered depth, it is necessary to calculate also the volume of the sputtered material. In order to do so, the *density* of the sputtered material shall be known. This can be estimated from the elemental composition and the densities of the pure elements.

There are two existing methods to calculate the sputtered depth, both of which can be utilised for the purposes of this standard method.

A.3.2 Calculation based on fractional volumes

For each segment, j, of the depth profile, calculate the sputtered volume, V_j, using the equation:

$$V_i = \sum_i \frac{m_{ij}}{\rho i} \qquad (A.13)$$

where

ρ_I is the density of element i.

For each segment, j, of the depth profile, calculate the depth, D_j, of that segment relative to the sample surface using the equation:

$$D_j = \sum_j \frac{V_j}{A_s} \qquad (A.14)$$

where

A_s is the area of the sputtered spot.

A.3.3 Calculation based on averaged density

For each segment, j, of the depth profile, calculate the atomic fraction, a_{ij}, using the equation:

$$a_{ij} = \frac{\left(\frac{c_{ij}}{w_i}\right)}{\sum_i \frac{c_{ij}}{w_i}} \tag{A.15}$$

where

w_i is the atomic mass of element i.

For each segment, j, of the depth profile, calculate the estimated density, ρ_j, using the equation:

$$\rho_j = \sum_i a_{ij} \times \rho_i \tag{A.16}$$

For each segment, j, of the depth profile, calculate the sputtered volume, V_j using to the equation:

$$Vj = \left(\frac{\sum_i m_{ij}}{\rho_j}\right) \tag{A.17}$$

Calculate the sputtered depth, D_j, using Equation (A.14) of A.3.2.

NOTE 1 In order to determine the sputtered depth accurately, it is essential to have an accurate value of the area of the sputtered spot *A* in Equation (A.14). In most commercial software for quantification of GD-OES depth profiles. A is simply calculated from the nominal diameter of the hollow anode of the glow discharge source (e.g. 4 mm or 8 mm). This estimate is often not accurate enough, and it is therefore essential to measure accurately the actual diameter of the sputtered spot for each device and anode used.

NOTE 2 In A.2.2, the calculation step that gives the actual sputtering rate of each segment, j, is strictly speaking not necessary. It is possible to calculate the sputtered mass per element according to a simpler algorithm. However, the sputtering rate is a parameter that often is of considerable analytical interest, which is the reason for introducing this as an intermediate calculation step.

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