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Surface chemical analysis — Analysis of zinc- and/or aluminium-based metallic coatings by glow-discharge optical-emission spectrometry

National foreword

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

This second edition cancels and replaces the first edition (ISO 16962:2005), which has been technically revised.

Introduction

This document is a revision of ISO 16962. Developments in both GD-OES instrumentation and the types of zinc- and/or aluminium-based metallic coatings currently produced have rendered ISO 16962 partly obsolete, and this revision is intended to bring it up to date.

Surface chemical analysis — Analysis of zinc- and/or aluminium-based metallic coatings by glow-discharge optical-emission spectrometry

1 Scope

This document specifies a glow-discharge optical-emission spectrometric method for the determination of the thickness, mass per unit area and chemical composition of metallic surface coatings consisting of zinc- and/or aluminium-based materials. The alloying elements considered are nickel, iron, silicon, lead and antimony.

This method is applicable to zinc contents between 0,01 mass % and 100 mass %; aluminium contents between 0,01 mass % and 100 mass %; nickel contents between 0,01 mass % and 20 mass %; iron contents between 0,01 mass % and 20 mass %; silicon contents between 0,01 mass % and 15 mass %; magnesium contents between 0,01 mass% and 20 mass%; lead contents between 0,005 mass % and 2 mass %, antimony contents between 0,005 mass % and 2 mass %.

NOTE Due to environmental and health risks, lead and antimony are avoided nowadays, but this document is also applicable to older products including these elements.

2 Normative references

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

ISO 14284, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*

ISO 17925, *Zinc and/or aluminium based coatings on steel — Determination of coating mass per unit area and chemical composition — Gravimetry, inductively coupled plasma atomic emission spectrometry and flame atomic absorption spectrometry*

3 Terms and definitions

No terms and definitions are listed in this document.

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

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

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

4 Principle

The analytical method described here involves the following processes:

a) preparation of the sample to be analysed, generally in the form of a flat plate or disc of dimensions appropriate to the instrument or analytical requirement (round or rectangular samples with a width of more than 5 mm, generally 20 mm to 100 mm, are suitable);

b) cathodic sputtering of the surface coating in a direct current or radio frequency glow-discharge device;

c) excitation of the analyte atoms in the plasma formed in the glow-discharge device;

d) spectrometric measurement of the intensities of characteristic emission spectral lines of the analyte atoms and ions as a function of sputtering time (qualitative depth profile);

e) 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.

5 Apparatus

5.1 Glow-discharge optical-emission spectrometer

5.1.1 General

The required instrumentation includes an optical-emission spectrometer system consisting of a Grimm type[1] or similar glow-discharge source (direct current or radio frequency powered) and a simultaneous optical spectrometer as described in ISO 14707, capable of providing suitable spectral lines for the analyte elements. It is also common to combine this with a sequential spectrometer (monochromator), allowing the addition of an extra spectral channel to a depth profile measurement. An array-type detector, such as a charge coupled device (CCD) or a charge injection device (CID) can also be used for simultaneous detection to cover a wide spectral range of the analytical lines.

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

Since the principle of determination is based on continuous sputtering of the surface layer, the spectrometer shall be equipped with a digital readout system for time-resolved measurement of the emission intensities. A system capable of a data acquisition speed of at least 300 measurements/second per spectral channel is recommended, but for a large number of applications speeds of > 50 measurements/second per spectral channel are acceptable. In practice, it has been established that 10 to 100 measurements/second per spectral channel are suitable.

5.1.2 Selection of spectral lines

For each analyte to be determined, there exist 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, the analyte mass fraction range, the sensitivity of the spectral lines and any spectral interference from other elements present in the test specimens. For applications where several of the analytes of interest are major elements in the specimens, special attention shall be paid to the occurrence of self-absorption of certain highly sensitive spectral lines (so-called “resonance lines”). Self-absorption causes non-linear calibration curves at high analyte mass fraction levels, and strongly self-absorbed lines should therefore be avoided for the determination of major elements. Suggestions concerning suitable spectral lines are given in Annex B. Spectral lines other than those listed may be used, so long as they have favourable characteristics.

5.1.3 Selection of glow-discharge source type

5.1.3.1 Anode size

Most GD-OES instruments on the market are delivered with options to use various anode diameters, 2 mm, 4 mm and 8 mm being the most common. Some older instruments have one anode only, usually 8 mm, while the most commonly used anode in modern instruments is 4 mm. A larger anode requires larger specimens and higher power during analysis; therefore, the specimen is heated to a greater extent. On the other hand, a larger anode gives rise to a plasma of larger volume that emits more light, resulting in lower detection limits (i.e. higher analytical sensitivity). Furthermore, a larger anode helps to mask inhomogeneity within a surface layer. This may or may not be an advantage, depending on the application. In a large number of applications, the 4 mm anode is a good compromise. However, in surface analysis applications, it is rather common to encounter problems of overheating of the specimens due to surface layers of poor heat conductivity and/or very thin specimens, for example. In such cases, a smaller anode (typically 2 or 2,5 mm) is preferable, even if there is some loss of analytical sensitivity.

5.1.3.2 Type of power supply

The glow-discharge source can be either a type powered by a direct current (DC) power supply or a radio frequency (RF) type. The most important difference is that the RF type can sputter both conductive and non-conductive specimens; hence, this is the only type that can be used for polymer coatings and insulating oxide layers, for example. On the other hand, it is technically simpler to measure and control the electrical source parameters (voltage, current, power) of a DC type. Several commercially available GD-OES systems can be delivered with the option to switch between DC and RF operation, but RF-only systems are becoming increasingly common. In short, there are a very large number of applications where DC or RF sources can be used and several where only an RF source can be used.

5.1.3.3 Mode of operation

Both DC and RF sources can be operated in several different modes with respect to the control of the electrical parameters (current, voltage, power) and the pressure. There are several reasons for this:

- "historical" reasons (older instruments have simpler but functional power supplies, while the technology has evolved, so newer models have more precise and easier-to-operate source control);
- different manufacturers have chosen different solutions for source control;
- there are some application-related issues where a particular mode of operation is to be preferred.

This document gives instructions for optimizing the source parameters based on several available modes of operation. The most important reason for this is to make these instructions comprehensive so as to include several types of instruments. In most applications, there is no major difference between these modes in terms of analytical performance, but there are other differences in terms of practicality and ease of operation. For instance, a system equipped with active pressure regulation will automatically be adjusted to the same electrical source parameters every time a particular analytical method is used. Without this technology, some manual adjustment of the pressure to achieve the desired electrical source parameters is normally required.

NOTE In this context, what is known as the emission yield[2][3][4][7] forms the basis for calibration and quantification as described in this document. The emission yield has been found to vary with the current, the voltage and, to a lesser extent, the pressure[4][7]. It is impossible in practice to maintain all three parameters constant for all test specimens, due to variations in the electrical characteristics of different materials. In several instrument types, the electrical source parameters (the plasma impedance) can therefore be maintained constant by means of automatic systems that vary the pressure during analysis. Alternatively, there exist methods to correct for impedance variations by means of empirically derived functions[4][7], and this type of correction is implemented in the software of commercially available GD-OES systems.

6 Adjusting the glow-discharge spectrometer system settings

6.1 General

Follow the manufacturer's instructions or locally documented procedures for preparing the instrument for use.

For the optical system, the most important preparation step is to 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 optimum signal-to-background ratio and good reproducibility. For further information, see ISO 14707.

The most important step in developing a method for a particular application is to optimize the parameters of the glow-discharge source. The source parameters shall be chosen to achieve three aims:

a) adequate sputtering of the test specimen, to reduce the analysis time without overheating the specimen;

b) good crater shape, for good depth resolution;

c) constant excitation conditions in calibration and analysis, for optimum accuracy.

Trade-offs are often necessary among the three specified aims. More detailed instructions on how to adjust the source parameters are given in 6.2 and 6.3.

The settings of the high voltage for the detectors depend on the source parameters, but the procedure is the same for all modes of operation of the source. This procedure is therefore only described for the first mode of operation.

Similarly, the steps to adjust and optimize the source settings in terms of signal stability and sputter crater shape are also similar in principle for all modes of operation. Therefore, these procedures are only described in detail for the first mode of operation.

NOTE There is no difference between DC and RF concerning the possibilities to measure the pressure. However, there are large pressures differentials in a Grimm type source, and pressure readings obtained depend on the location of the pressure gauge. Some instrument models have a pressure gauge attached to measure the actual pressure in the plasma, while others have a pressure gauge located on a “low pressure” side of the source closer to the pump. Therefore, the pressure readings can, for several instruments, just be used to adjust the source parameters of that particular instrument, not as a measure of the actual operating pressure in the plasma.

6.2 Setting the parameters of a DC source

6.2.1 Constant applied current and voltage

6.2.1.1 General

The two control parameters are the applied current and the applied voltage. Set the power supply for the glow-discharge source to constant current/constant voltage operation (current set by the power supply, voltage adjusted by pressure/gas flow regulation). Then, set the current and voltage to the typical values recommended by the manufacturer. Alternatively, set the power supply to constant voltage/constant current operation (voltage set by the power supply, current adjusted by pressure/gas flow regulation). If no recommended values are available, set the voltage to 700 V and 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 or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range.

NOTE For the purposes of this document, there is no difference between the two alternative modes of operation described above. However, for applications to very thin films, there may be a small difference in the very short start-up of the discharge, affecting the analytical results to some extent.

6.2.1.2 Setting the high voltage of the detectors

Select test specimens with surface layers of all types to be determined. For all test specimens, run the source while observing the output signals from the detectors for the analyte atoms. Adjust the high voltage of the photomultiplier (PMT) detectors in such a way that sufficient sensitivity is ensured at the lowest analyte mass fraction without saturation of the detector system at the highest analyte mass fraction. For array type detectors (CCD or CID), adjust the integration time in the same way as the high voltage for PMT.

6.2.1.3 Adjusting the source parameters

For each type of test specimen, carry out a full-depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the surface layers 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. If this is found not to be the case, reduce one of the control parameters by a small amount and sputter through the surface layers 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.

NOTE Unstable emission signals could indicate thermal instability in the specimen surface layers; specimen cooling is beneficial in this regard.

6.2.1.4 Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a specimen with a surface layer typical of the test specimens to be analysed to a depth of about 10 µm to 20 µm, but still inside the surface layer. This is only possible for application where surface layers of such thickness are available. If no such specimen is available, use a steel or brass specimen. Measure the crater shape by means of the profilometer device. Repeat this procedure a few times using slightly different values of one of the control parameters. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis, provided that the stability of the emission conditions obtained in step 6.2.1.3 is not compromised. In some cases, there is a certain trade-off between these two requirements.

6.2.2 Constant applied current and pressure

The two control parameters are the applied current and the pressure. Set the power supply for the glow-discharge source to constant current operation. Then, 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 or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range. Sputter a typical coated test specimen, and adjust the pressure until a voltage of approximately 700 V is attained in the surface layer.

Set the high voltage of the detectors as described in 6.2.1.2.

Adjust the source parameters as described in 6.2.1.3, adjusting first the current and, if necessary, the pressure.

Optimize the crater shape as described in 6.2.1.4 by adjusting the pressure. These conditions are then used during calibration and analysis.

NOTE Before sputtering a new specimen type, make a test run in order to ensure that the voltage has not changed by more than 5 % from the previously selected value. If this is the case, readjust the pressure until the correct value is attained.

6.2.3 Constant voltage and pressure

The two control parameters are applied voltage and pressure. Set the power supply for the glow-discharge source to constant voltage operation. First, set the voltage to a typical value recommended by the manufacturer. If no recommended values are available, set the voltage to 700 V. Sputter a typical coated test sample, and adjust the pressure until a current is attained 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 in the surface layers. If no previous knowledge about the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range.

Set the high voltage of the detectors as described in 6.2.1.2.

Adjust the source parameters as described in 6.2.1.3, adjusting first the voltage and, if necessary, the pressure.

Optimize the crater shape as described in 6.2.1.4, by adjusting the pressure. These conditions are then used during calibration and analysis.

NOTE Before sputtering a new sample type, make a test run in order to ensure that the current 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.

6.3 Setting the discharge parameters of an RF source

6.3.1 General

The most common operating modes of RF sources are the following: constant applied power and constant pressure; constant applied voltage and constant pressure; or constant effective power and applied voltage. All RF operational modes are allowed in this document, provided they meet the three aims listed in 6.1. In the following, separate instructions are provided on how to set the parameters for the different operational modes.

NOTE RF sources differ from DC sources in the respect that for several instrument models, only the applied (forward) RF power can be measured, not the actual power developed in the glow-discharge plasma. The applied RF power is normally in the range 10 W to 100 W, but it must be noted that the RF power losses in connectors, cables, etc. vary considerably between different instrument models and the point of contact of the RF power to the sample. Typical power losses are in the range 10 % to 50 % of the applied power. Furthermore, the possibilities to measure the additional electrical parameters voltage and current in the plasma are more or less restricted due to technical difficulties with RF systems, and several existing instrument models can only measure the applied RF power.

6.3.2 Constant applied power and pressure

The two control parameters are the applied power and the pressure. First, set the applied power and adjust the source pressure to the values suggested by the manufacturer. If recommended values are not available, set the applied power and pressure to somewhere in the middle of the ranges available for the instrument used. Measure the penetration rate (i.e. depth per unit time) on an iron or steel specimen, adjusting the power to give a penetration rate of about 2 µm/min to 3 µm/min.

Set the high voltage of the detectors as described in 6.2.1.2.

Adjust the source parameters as described in 6.2.1.3, adjusting first the applied power and, if necessary, the pressure.

Optimize the crater shape as described in 6.2.1.4 by adjusting the pressure.

Remeasure the penetration rate on the iron or steel specimen and adjust the applied power, if necessary, to return to about 2 µm/min to 3 µm/min. Repeat the cycle of power and pressure adjustment until no significant change is noted in the penetration rate or crater shape. Note the power and pressure used in units provided for the instrument type. These conditions are then used during calibration and analysis.

6.3.3 Constant applied power and DC bias voltage

The two control parameters are the applied power and the DC bias voltage. First, set the applied power and adjust the source pressure to attain a DC bias typical of the values suggested by the manufacturer. If recommended values are not available, set the applied power and DC bias voltage to somewhere in the middle of the range commonly used for depth profiling of metal specimens. On instruments equipped with active pressure control, this can be achieved automatically. Measure the penetration rate (i.e. depth per unit time) on an iron or steel specimen, adjusting the power to give a penetration rate of about 2 µm/min to 3 µm/min.

Set the high voltage of the detectors as described in 6.2.1.2.

Adjust the discharge parameters as described in 6.2.1.3, adjusting first the applied power and, if necessary, the DC bias voltage.

Optimize the crater shape as described in 6.2.1.4 by adjusting the DC bias voltage.

Remeasure the penetration rate on the iron or steel specimen and adjust the applied power, if necessary, to return to about 2 µm/min to 3 µm/min. Repeat the cycle of power and DC bias voltage adjustment until no significant change is noted in the penetration rate or in the crater shape. If this is not the case, readjust the DC bias voltage until the correct value is attained. Note the power and DC bias voltage used in units provided for the instrument. These conditions are then used during calibration and analysis.

6.3.4 Constant effective power and effective RF voltage

The two control parameters are the effective power and the RF voltage. Constant effective power is defined here as the applied power minus the reflected power and the "blind power" measured with the specimen in place but without plasma (vacuum conditions). The RF voltage is defined here as the RMS voltage at the coupling electrode without DC bias[8][9].

Set the power supply for the glow-discharge source to constant effective power/constant RF voltage operation. First, set the power to a typical value recommended by the manufacturer. If no recommended values are available, set the RF voltage to 700 V and the power to a value in the range 10 W to 15 W for a 4 mm anode, 5 to 10 W for a 2 mm anode to give an example. If no previous knowledge of the optimum power is available, it is recommended to start with a value somewhere in the middle of the recommended range.

Set the high voltage of the detectors as described in 6.2.1.2.

Adjust the discharge parameters as described in 6.2.1.3, adjusting first the effective power and, if necessary, the RF voltage.

Optimize the crater shape as described in 6.2.1.4 by adjusting the RF voltage. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

6.4 Minimum performance requirements

6.4.1 General

It is desirable for the instrument to conform to the performance specifications given in 6.3.2 and 6.3.3 below.

NOTE Setting up for analysis commonly requires an iterative approach to the adjustment of the various instrumental parameters described in this document.

6.4.2 Minimum repeatability

The following test shall be performed in order to check that the instrument is functioning properly in terms of repeatability.

Perform 10 measurements of the emission intensity on a homogeneous bulk specimen with a content of the analyte exceeding a mass fraction of 1 %. The glow-discharge conditions shall be those selected for analysis. These measurements shall be performed using a discharge stabilization time (often referred to as "preburn") of at least 60 s and a data acquisition time in the range 5 s to 20 s. Each measurement shall be located on a newly prepared surface of the specimen. Calculate the relative standard deviation of the 10 measurements. The relative standard deviation shall conform to any requirements and/or specifications relevant to the intended use.

NOTE Typical relative standard deviations determined in this way are 2 % or less.

6.4.3 Detection limit

6.4.3.1 General

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 surface layers 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-fifth of the lowest expected mass fraction in the surface layer to be analysed.

6.4.3.2 SNR method

The first method is often called the “signal-to-noise ratio (SNR) method”. In order to evaluate the detection limit for a given analyte, the following steps are performed.

Select a bulk specimen to be used as a blank. The composition of the specimen should preferably be similar, in terms of the elemental composition of the matrix, to that of the surface layers to be analysed. Further, the specimen shall be known to contain less than 1 μg/g of the analyte.

Perform 10 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 preferably be the same as those that will be used in the analysis of the coated specimens. For each measurement, the blank shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use an unsputtered area of the surface of the blank for each individual burn.

Compute the detection limit, expressed as a mass fraction, using Formula (1):

$$\mathrm{DL} = \frac{3 \times \sigma}{S} \tag{1}$$

where

DL is the detection limit;

σ is the standard deviation of the background intensity measurements performed in step 2;

S is the analytical sensitivity derived from the instrument calibration, expressed in the appropriate units (the ratio of intensity to mass fraction).

If the detection limit calculated is unacceptable, the test shall be repeated. If the second value calculated is also unacceptable, then the cause shall be investigated and corrected prior to analysing specimens.

6.4.3.3 SBR-RSDB method

The second method, which does not require a blank, is often called the “signal-to-background ratio — relative standard deviation of the background (SBR-RSDB) method”. The method is performed as follows.

a) Select a bulk specimen which has a matrix composition that is similar to that of the surface layers to be analysed and in which the mass fraction of the analyte is greater than 0,1 % and accurately known. If an analytical transition that is prone to self-absorption (see 5.1.2) is to be used, the mass fraction of the analyte should preferably not exceed 1 %.

b) Perform three replicate burns on the chosen specimen. For each burn, integrate the emission intensity at the analytical wavelength for 10 s. The glow-discharge conditions used shall be similar to those that will be used in the analysis of the coated specimens. For each measurement, the specimen shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use a freshly prepared area of the surface of the specimen for each individual burn. Average the three replicate emission intensities.

c) Select a peak-free region of the emission spectrum within 0,2 nm of the analytical peak. Perform ten replicate burns on the chosen specimen. For each burn, integrate the intensity at the peak-free region for 10 s. These are the measurements of the background intensity. The glow-discharge conditions and preburn shall be the same as those used in step 2. Once again, use a freshly prepared area of the surface of the specimen for each individual burn. Compute the average and the relative standard deviation of the ten replicate measurements.

d) Calculate the detection limit using Formula (2):

$$\mathrm{DL} = \frac{3\times\left(w_{\mathrm{A}}\times\sigma_{\mathrm{R\,el,B}}/100\right)}{\left(I-I_{\mathrm{B}}\right)/I_{\mathrm{B}}} \tag{2}$$

where

DL is the detection limit;

w_{A} is the mass fraction of the analyte in the specimen;

$\sigma_{\mathrm{Rel,B}}$ is the relative standard deviation of the background from step 3, expressed as a percentage;

I_{B} is the average background intensity from step 3;

I is the average peak intensity from step 2.

If the detection limit calculated is unacceptable, then the test shall be repeated. If the second value calculated is also unacceptable, then the cause shall be investigated and corrected prior to analysing specimens.

7 Sampling

Carry out sampling in accordance with ISO 14284 and/or relevant national/international standards, as appropriate. If no such standards are available, follow the instructions from the manufacturer of the coated material or another appropriate procedure. The edges of a coated strip should preferably be avoided. The size of the test specimens taken shall be suitable for the glow-discharge source used. Typically, round or rectangular specimens with sizes (diameter, width and/or length) of 20 mm to 100 mm are suitable. This is due to the fact that diameter of the sealing o-ring of the source typically is in the range 8 mm to 20 mm, and it is desirable to have sufficient area to make at least two replicate measurements on each specimen.

Rinse the surface of the specimen with an appropriate solvent (high-purity acetone, ethanol or n-heptane) to remove oils. Blow the surface dry with a stream of inert gas (argon or nitrogen) or clean, oil-free compressed air, being careful not to touch the surface with the gas delivery tube. The wetted surface may be lightly wiped with a wetted, soft, lint-free cloth or paper to facilitate the removal of oils. After wiping, flush the surface with solvent and dry as described above.

8 Calibration

8.1 General

Calibration of the system consists of determining, for each analyte and spectral line, the analytical response curve as described in either A.2 or A.3. In order to carry out the calibration, it is necessary to know both the chemical composition and the sputtering rates (mass loss rates) of the calibration samples.

8.2 Calibration samples

8.2.1 General

Whenever possible, spectrometric calibration samples issued as Certified Reference Materials (CRMs) 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 well determined and reproducible. High-purity metals are very useful for the determination of the spectral backgrounds in regions of the spectrum where they do not have emission lines. However, they are not always recommended for the purpose to calibrate for high mass fraction since the metals with melting points <800 K, e.g. Zn, Sn and Pb, have poor repeatability of sputtering rates and intensities. The following considerations are the most important in the selection of the calibration samples.

a) There shall be at least three calibration samples for each analyte, covering a range from zero to the highest mass fraction to be determined. This is a minimum requirement, at least five calibration samples are recommended whenever possible.

b) The samples shall be homogeneous to the extent that the mass sputtered during a calibration measurement is representative of the given composition.

Based on these general recommendations, the following types of calibration samples are suggested. Additional calibration samples of other alloy types containing the analytes may be used.

8.2.2 Brass calibration samples

Select at least two brass samples with zinc mass fractions of 25 % to 50 %; aluminium mass fractions of 1 % to 4 %; lead mass fractions of 1 % to 4 %.

8.2.3 Zn-Al alloy samples

Select at least two Zn-Al alloy samples with zinc mass fractions of 40 % to 90 %.

8.2.4 Low alloy iron or steel samples

Select at least two low alloy iron or steel samples with greater iron mass fraction than 98 %. The iron mass fraction may be determined by subtracting the sum of the mass fractions for all other known elements from 100 %.

8.2.5 Stainless steel samples

Select at least two stainless steels with nickel mass fractions of 10 % to 40 %.

8.2.6 Nickel alloy samples

Select at least one nickel based alloy sample with a higher nickel mass fraction than 70 % (a higher Ni mass fraction than the 20 % defined in the scope is necessary due to the high sputtering rate of the Zn-Ni alloys; the calibration points being defined by the product of sputtering rate and mass fraction).

8.2.7 Aluminium-silicon alloy samples

Select at least one aluminium-silicon alloy sample with silicon mass fractions of 5 % to 10%.

8.2.8 Aluminium-magnesium alloy samples

Select at least one aluminium-silicon alloy sample with magnesium mass fractions of 3 % to 10 %.

8.2.9 High-purity copper and zinc samples

Select a high-purity copper and/or high-purity zinc sample with mass fractions of the analytes less than 0,001 %. These samples can be used to establish the zero points of the calibrations for all analytes except copper and zinc. The reason to use these samples rather than pure iron is that both copper and zinc have spectra dominated by just a few emission lines, and very low background levels in most parts of the optical spectrum.

8.3 Validation samples and optional RMs for calibration

8.3.1 General

Validation (see 8.7) samples should be prepared in order to check the accuracy of the analytical results. The following sample types are suggested, but other samples may be used where appropriate. These samples may also be used as additional calibrants.

8.3.2 Zinc-nickel electrolytically coated RM

Electrolytically coated RM with nickel mass fraction less than 20 %. The coating mass per unit area and chemical compositions of coated RM shall be determined by reference methods specified by such as ISO 17925.

8.3.3 Zinc-iron electrolytically coated RM

Electrolytically coated RM with zinc mass fraction higher than 30 % and iron mass fraction higher than 5 %. The coating areic mass per unit area and chemical compositions of coated RM shall be determined by reference methods specified by such as ISO 17925.

8.3.4 Zinc-aluminium hot dip coated RM

Zinc-aluminium hot dip coated RM with zinc mass fraction higher than 10 % and aluminium mass fraction higher than 5 %. The chemical compositions of coated RM shall be determined by reference methods specified by such as ISO 17925.

8.3.5 Zinc-iron hot dip coated and annealed RM

Zinc-iron hot dip coated and annealed RM with iron mass fraction about 10 %. The chemical compositions of coated RM shall be determined by reference methods specified by such as ISO 17925.

NOTE 1 Reference Material (RM): Material or substance one or more of whose property values are sufficiently homogeneous, stable and well established to be used for the calibration of an apparatus, the assessment of a measurement method or for assigning values to materials.

NOTE 2 Certified Reference Material (CRM): Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence. By trademark, a Standard Reference Material®1) (SRM®) is a CRM issued by the National Institute of Standards and Technology, Gaithersburg, MD, USA.

8.4 Determination of the sputtering rate of calibration and validation specimens

The term “sputtering rate” is understood here to be equivalent to the mass loss rate during sputtering in the glow discharge. The term “relative sputtering rate” is understood here to be the sputtering rate of the specimen divided by the sputtering rate of a reference material sputtered under the same

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1) Standard Reference Material is the trademark of a product supplied by the National Institute of Standards and Technology. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

conditions. If the sputtered areas of the specimen and the reference specimen are the same, then the relative sputtering rate is equivalent to the relative sputtering rate per unit area. Proceed with sputtering rate determinations as follows:

a) prepare the specimen surface in accordance with the recommendations of the instrument manufacturer or using another appropriate procedure;

b) adjust the glow-discharge parameters to those selected by following the procedure in 6.2 or 6.3;

c) sputter the specimen 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 specimen 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 four profile traces in different directions across the centre of the crater;

f) for absolute sputtering rates:

    1) measure the area of at least one crater,

    2) calculate the sputtered volume of each crater by multiplying the sputtered area by the average sputtered depth,

    3) calculate the sputtered mass as the volume multiplied by the density of the specimen,

    4) calculate the sputtering rate for each crater as the mass loss divided by the total sputtering time,

    5) calculate the average sputtering rate and the standard deviation from the measurements of each crater;

g) for relative sputtering rates:

    1) calculate the sputtered mass per unit area for each crater as the sputtered depth multiplied by the density of the specimen,

    2) calculate the sputtering rate per unit area for each crater as the sputtered mass per unit area divided by the total sputtering time,

    3) choose a reference specimen (iron or low-alloy steel similar to NIST 1761 is recommended) and measure the average sputtering rate per unit area for this reference specimen as described above for the calibration specimens,

    4) calculate the relative sputtering rate for each crater as the sputtering rate per unit area divided by the average sputtering rate per unit area of the reference,

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

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

NOTE 1 The true average sputtered depth is not exactly identical to the average depth of a line scan through the centre of the crater, but an average of all data of the sputtered area. Techniques based on 3D measurements of the crater volume have been developed, using advanced profilometer systems[9][10].

NOTE 2 The sputtered mass can also be determined by weighing specimens before and after sputtering. However, this requires the use of scales of extremely high accuracy, and the uncertainty in such measurements is generally inferior to that with crater depth measurements.

NOTE 3 The sputtering rates of certain RMs might be available from the instrument manufacturer.

If laboratory means are available, measure the density of each calibration specimen. A suitable method for homogeneous specimens is specimen mass divided by specimen volume, where the specimen volume is measured by immersion of the specimen in water following the method of Archimedes. Alternatively, the specimen volume can be estimated from the specimen dimensions or the density calculated from the specimen composition as described in Annex A [see Formula (A.34)]. The accuracy of the measured or calculated density should be better than 5 %.

8.5 Emission intensity measurements of calibration specimens

The procedure for measuring the calibration specimens is as follows.

a) Prepare the surfaces of the calibration specimens in accordance with the instrument manufacturer's instructions. If such instructions are not available, dry grinding with 220 grit abrasive paper is usually sufficient for any bulk specimen. However, wet grinding may be beneficial. Wet specimens can be dried by thoroughly rinsing them with ethanol and then blow the surface dry with a stream of inert gas (argon or nitrogen) or clean, oil-free compressed air, being careful not to touch the surface with the gas delivery tube.

b) Adjust the source parameter settings to those selected in 6.2 or 6.3. Choose a preburn time of 50 s to 200 s and a signal integration time of 5 s to 30 s.

c) Measure the emission intensities of the analytes. The unit in which the intensities are given is of no importance. Commonly used units are counts per second (cps) and volts (V). Measure each specimen at least two times and calculate the average values.

8.6 Calculation of calibration equations

Perform the calibration computations in accordance with one of the calculation methods specified in Annex A. The software for all commercially available GD-OES instruments incorporates at least one of these calculation methods.

8.7 Validation using reference materials

8.7.1 General

Carry out the following procedure immediately after calibration in order to confirm that the calibration equations are accurate. This process is called "validation of calibration" (see the Note). It is not necessary to validate the calibration every time a new specimen is analysed. A related procedure (verification) shall be used on a more routine basis to check for instrument drift over time, as described in 8.8.

Two validation procedures are described below. The first procedure (see 8.7.2) makes use of bulk reference materials and the second (see 8.7.3) employs surface layer reference materials. Such surface layer reference materials are often difficult to obtain. As a result, the validation procedure described in 8.7.3 is optional.

NOTE Validation is the confirmation, through the provision of objective evidence, that the particular requirements for a specific intended use or application have been fulfilled (cited from ISO 9000:2015, 3.8.5). Validation of a method is defined in ISO/IEC 17025:2005, 5.4.5. Validation of the calibration is analogous to it (cf. the Note in 8.8).

8.7.2 Checking analytical accuracy using bulk reference materials

a) Select, in accordance with 8.1, an appropriate number of bulk reference materials to be used for validation of the calibration.

b) Measure the emission intensities of these validation specimens under the same source conditions and using the same preburn and integration times as selected for calibration. At least three independent burns shall be made on each specimen, using a freshly prepared surface for each burn.

c) Compute the average mass fractions of the analytes for each validation specimen, based upon the calibration equations.

d) Confirm that the average mass fractions of the analytes measured in this way agree with known values to within appropriate statistical bounds. If statistically significant disagreement is found, the disagreement shall be investigated. It might be necessary to repeat the calibration.

8.7.3 Checking analytical accuracy using surface layer reference materials

a) Follow the instrument manufacturer's instructions for setting up the depth profile analysis.

b) Use the same source operating parameters as those used to establish the calibration.

c) Sputter each surface layer reference material for a sufficiently long time to ensure that the surface layer is completely removed and sputtering has continued well into the substrate.

d) Compute the mass fractions of the analytes versus depth using the calibration equations. The instrumental software can normally be set to automatically calculate this relationship at the end of each analysis.

e) Calculate the total mass of surface layer in g/m^2, including all major analytes of the coating. The software of most commercially available instruments has a convenient function for this calculation. The difference between the assigned value and the calculated value shall not exceed ±5 %.

f) Calculate the coating depth in µm. The difference between assigned values for a reference material (RM) and the calculated value shall be ±5 % or better. The difference between assigned values for a chemically analysed commercial strip and the calculated value shall be within ±10 %.

g) If a profilometer is available, a one-time verification of the depth calculation can be made. If the assigned value, calculated value and profilometer value agree within appropriate statistical bounds, then the calibration equations are acceptable.

h) If the validation is not successful, the problem shall be investigated. It may be necessary to repeat the calibration.

8.8 Verification and drift correction

The analytical response of a spectrometric instrument might drift over time. Even if the instrument has just been calibrated and validated, it is necessary to verify that the calibration equations are still in control prior to determining unknown specimens in each working day or shift. If the instrument manufacturer has not provided a procedure for calibration verification, then the following procedure shall be performed:

a) Select a limited number of homogeneous test specimens to be used for verification of the calibration. These specimens should ideally have compositions that cover the relevant range of mass fractions of the elements to be analysed.

b) Measure the emission intensities of these specimens under the same discharge conditions and using the same preburn and integration times as selected for calibration. At least two independent burns shall be made on each specimen, using a freshly prepared surface for each burn.

c) Compute, using the calibration equations, the average mass fractions of the analytes for each specimen.

d) Confirm that the average mass fractions of the analytes measured in this way agree with known values to within appropriate statistical bounds. If statistical disagreement is found, carry out a drift correction by shifting the calibration equation or correcting the emission intensities, as specified by the instrument manufacturer.

It is recommended that a verification specimen be analysed after drift correction to prove the accuracy of the calibration equations.

NOTE Verification is the confirmation, through the provision of objective evidence, that specified requirements have been fulfilled (cited from ISO 9000:2015, 3.8.4; cf. also the Note in 8.7.1).

9 Analysis of test specimens

9.1 Adjusting discharge parameters

Adjust, as closely as possible, the source controls to give the same discharge conditions as those used during calibration of the analytical method.

9.2 Setting of measuring time and data acquisition rate

Care shall also be taken to select a total measuring time and data acquisition rate suitable for the type of test specimen analysed. In the software of all commercially available GD-OES systems, there are flexible provisions for variation of the acquisition rate; in most cases, the measuring time can also be subdivided into sections with different data acquisition rates. The acquisition rates are determined from the time needed to sputter through the typical thickness of the surface layers of the specimens. It should be remembered that a very high rate results in very short integration times, leading to more noisy signals. As a general recommendation, a layer or other feature in the depth profile should include at least 10 data points. It is often advisable to have a subdivision of at least two time intervals, using a high acquisition rate initially in order to resolve rapidly changing features in the top surface layer, then to decrease the rate in order to improve the signal-to-noise ratio of the signals.

As an example, suppose the specimen has a very thin surface layer of thickness 5 nm and the sputtering rate is 50 nm/s. It is advisable to maintain a high acquisition rate to a depth at least twice the layer thickness, in this case 10 nm. This means maintaining a high acquisition rate for at least 0,2 s and collecting at least 20 data points during this time. This means that the minimum initial data acquisition rate has to be 100 measurements/second. Due to the fact that the depth resolution deteriorates with sputtered depth, the acquisition rate can be successively decreased without loss of depth information. The most suitable settings have to be determined for each application.

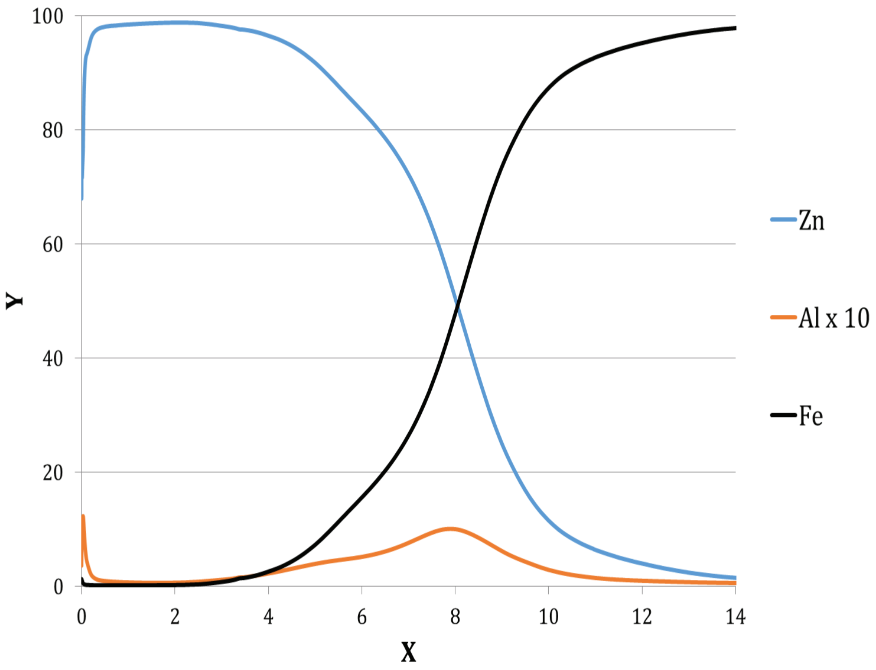
9.3 Quantifying depth profiles of test specimens

Calculate quantified depth profiles, using the calibration equations established in accordance with Clause 8, in accordance with one of the calculation procedures described in Annex A.

10 Expression of results

10.1 Expression of quantitative depth profile

Examples of quantitative depth profiles are shown in Figure 1 and Figure 2.

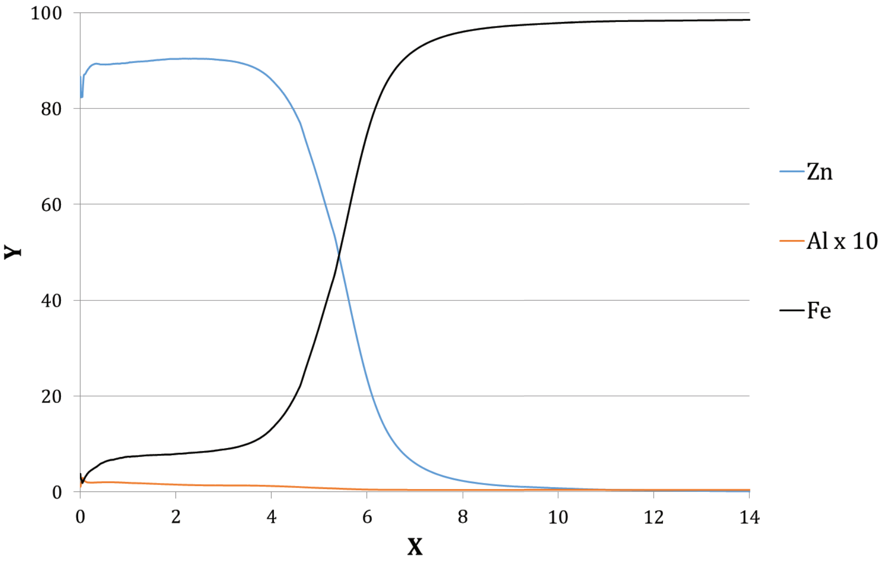


Key

X depth (µm)

Y mass fraction (%)

Figure 1 — Quantitative depth profile of a hot dipped ZnAl coating on steel



Key

X depth (µm)

Y mass fraction (%)

Figure 2 — Quantitative depth profile of a Galvanneal ZnFe coating on steel

10.2 Determination of total coating mass per unit area (coating aeric mass)

10.2.1 General method

In cases where the surface layers consist entirely of elements present in very low concentrations in the substrate material (e.g. a ZnAl coating on a steel substrate), the coating aeric mass can be calculated by integration of the depth profile for each element. This is a rather straightforward calculation, since the mass fraction/element/depth segment is available from the quantitative depth profile, and most commercial instruments have software to perform such calculations. It is important to carry out the integration for elements present in the surface layers only.

The following general recommendation for determination of the integration depth is given:

a) define the surface layer thickness as the distance from the surface to the depth at which the mass fraction of a selected major surface layer element is reduced to 50 % of the "plateau" value in the surface layer;

b) define the width of the interface as the difference between the two points in depth where the mass fractions of the selected major element are 84 % and 16 % of the "plateau" value in the surface layer. The "plateau" value must be estimated by the analyst in cases where the surface layer is not quite homogeneous or very thin;

c) the integration depth is the sum of the surface layer thickness and the interface width.

10.2.2 Method for special applications

In cases where a major element of the surface layer is the same as that of the substrate (e.g. iron oxide on a steel substrate), there exist special calculation methods for certain applications, described in Annex C.

10.3 Determination of average mass fractions

The average mass fraction of each element in the surface layer is determined by dividing the integrated aeric mass per unit area for the element (within the integration depth according to 9.2) by the total surface layer aeric mass per unit area.

11 Precision

A planned trial of this method was carried out by four laboratories, for seven elements, each laboratory making two or more determinations of each element. The test samples used and mean results obtained are listed in Table D.1. The results obtained were treated statistically in accordance with ISO 5725-2. Two or more determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating condition, same calibration and a minimum period of time. Repeatability limit is calculated in accordance with ISO 5725-6. The data obtained are summarized in Table 1 and Table 2. The graphical representation of the figures is given in Annex D.

NOTE The precision obtained of hot-dip coated steel is mainly caused by inhomogeneity of samples in practice but not by measurement capability.

Table 1 — Results for repeatability standard deviation and repeatability limit of coating areic mass

Dimensions in g/m^2

Type of coating	Repeatability standard deviation s_r	Repeatability limit r = 2,8 times s_r
Electrolytic coating	0,75	2,1
Hot dip coating	4,5	16,0

Table 2 — Results for repeatability standard deviation and repeatability limit of mass fraction % in a coating

Element content	**Repeatability standard deviation** s_r	**Repeatability limit** **r = 2,8 times** s_r
Less than 0,1	0,006	0,017
1	0,03	0,084
10	0,2	0,56
99	1	2,8

12 Test report

It is recommended that the test report include the following information:

a) all information necessary for the identification of the sample;

b) the laboratory and the date of the analysis;

c) the method used, if relevant by reference to this document or another document;

d) the analytical results and the form in which they have been expressed;

e) any unusual features noted during the determination;

f) 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 General

All methods for calibration and quantitative evaluation of depth profiles in commercially available spectrometer systems are based on the concept of *emission yield* (EY), which can be defined as the emitted light of a spectral line per unit sputtered mass of the corresponding element[2][3]. The EY is an element- and instrument-dependent quantity, which must be determined independently for each spectral line and instrument. The assumption which forms the basis for this quantification technique is that the integrated signal intensity from one element (and spectral line) is proportional to just the sputtered mass of that element, which implies that the EY is independent of the sample composition (matrix). This has been investigated by several authors[4][5][6], and is by now widely accepted to be valid, at least to a first approximation. A few different mathematical models for calibration and quantification of intensity depth profiles have been developed based on the matrix-independent EY concept, therefore, the calculation steps in the software of different commercially available instruments are not identical. Furthermore, there exist a few types of correction algorithms for variations in the source discharge parameters, based on empirical models. More recently, correction algorithms for the influence of hydrogen on the EY have also been developed and incorporated in the software of commercial instruments. In the following, all know varieties of these quantification calculations are described in detail. It must be emphasized that they are all valid and acceptable for the purpose of this document, the relevant test of validity in an actual spectrometer system is the validation procedure described in 8.7. Any further development of quantification calculations will also be acceptable provided these validation procedures give satisfactory results.

A.2 Symbols

A.2.1 Symbols used generally in this annex

A_{ij}	atomic fraction of element i in segment j
$\mathrm{A_D}$	area of sputtering crater on specimen D
a_λ	constant describing the influence of current on the intensity of spectral line λ
b_λ	constant describing the influence of hydrogen on the intensity of spectral line λ
$I_{i\lambda}$	emission intensity at wavelength λ of element i
$I''_{i\lambda}$	emission intensity at wavelength λ of element i corrected for variations in discharge parameters
$I'''_{i\lambda}$	emission intensity at wavelength λ of element i corrected for the influence of hydrogen
I_H	observed hydrogen emission intensity
$\mathrm{I_{Href}}$	hydrogen emission intensity from a reference material, e.g. a TiH2 layer or a specific type of polymer

I_{HD}	hydrogen intensity recorded for calibration specimen D
$I_{\mathrm{B}\lambda}$	average background intensity at wavelength λ
$m_{i\mathrm{D}j}$	sputtered mass per unit area of element i in segment j of specimen D
$m_{j\mathrm{tot}}$	total sputtered mass per unit area in segment j
$r_{i\lambda}^{U}$	regression parameter in the calibration function
s_j	current in segment j
s_0	reference current given by the instrument manufacturer
s_{cal}	current used for the calibration of the method
U_j	voltage in segment j
U_0	threshold voltage for sputtering
U_{D}	voltage recorded for calibration specimen D
U_{av}	average voltage recorded for the set of calibration specimens used
U_{cal}	voltage used for the calibration of the method
$w_{i\mathrm{D}}$	mass fraction of element i in specimen D
$w_{i\mathrm{D}j}$	mass fraction of element i in depth segment j of specimen D
W_i	atomic mass of element i
z_j	thickness of segment j
Δt_j	time increment corresponding to depth segment j
ρ_i	density of pure element i
ρ_j	density of segment j

A.2.2 Symbols used in A.2 and A.6 concerned with relative sputtering rates

B_{λ}	spectral background term at wavelength λ, expressed as a mass fraction
$B_{\lambda\mathrm{rel}}$	related spectral background term at wavelength λ, expressed as a mass fraction
$e_{i\lambda}$	constant describing the degree of non-linearity for element i at spectral line λ
$k_{i\lambda}$	constant factor derived from the inverse emission yield (of element i at spectral line λ) divided by the relative sputtering rate
q_{D}	sputtering rate, expressed as a mass loss rate per unit area, of specimen D
q_{ref}	sputtering rate of a reference specimen (e.g. pure iron)

$q_{\mathrm{D}j}$	sputtering rate, expressed as a mass loss rate per unit area, in segment *j* of specimen D
$R_{i\lambda}$	inverse emission yield of element *i* at spectral line λ
$\mathfrak{R}_{i\lambda}$	emission yield of element *i* at spectral line λ

A.2.3 Symbols used in A.3 and A.7 concerned with absolute sputtering rates

B'_{λ}	spectral background term at wavelength λ, expressed as a mass fraction multiplied by the specimen sputtering rate
$B'_{\lambda\mathrm{rel}}$	related spectral background term at wavelength λ, expressed as a mass fraction
$e'_{i\lambda}$	constant describing the degree of non-linearity for element *i* at spectral line λ
$k'_{i\lambda}$	factor derived from the inverse emission yield divided by the sputtering rate
q'_{D}	sputtering rate of specimen D
$q'_{\mathrm{D}j}$	sputtering rate in segment *j* of specimen D
$R'_{i\lambda}$	inverse emission yield of element *i* at spectral line λ
$\mathfrak{R}'_{i\lambda}$	emission yield of element *i* at spectral line λ
$r^{\mathrm{H}}_{i\lambda}$	a regression parameter describing the influence of hydrogen on spectral line λ

A.3 Calculation of calibration constants using relative sputtering rates

Calibration is conducted using Formula (A.1) or Formula (A.2):

$$w_{i\mathrm{D}} \times \left(q_{\mathrm{D}} / q_{\mathrm{ref}}\right) = R_{i\lambda} \times I_{i\lambda} - B_{\lambda} \tag{A.1}$$

or

$$w_{i\mathrm{D}} = R_{i\lambda} \times I_{i\lambda} \times \left(q_{\mathrm{ref}} / q_{\mathrm{D}}\right) - B_{\lambda\mathrm{rel}} \tag{A.2}$$

where

$w_{i\mathrm{D}}$	is the mass fraction of element *i* in specimen D;
$q_{\mathrm{D}}/q_{\mathrm{ref}}$	is the sputtering rate of specimen D relative to that of a reference specimen;
q_{D}	is the sputtering rate expressed as the mass loss rate per unit area of specimen D;
q_{ref}	is the sputtering rate expressed as the mass loss rate per unit area of a reference specimen;
$R_{i\lambda}$	is the inverse emission yield of element *i* at spectral line λ (see also Note 1);
$I_{i\lambda}$	is the emission intensity at wavelength λ of element *i;*

B_λ	is a spectral background term at wavelength λ;
$B_{\lambda \mathrm{rel}}$	is a different but related spectral background term at wavelength λ which is expressed, in Formula (A.2), as a mass fraction and is often referred to as the "background equivalent concentration" (see also Note 2);
$q_{\mathrm{ref}}/q_{\mathrm{D}}$	is equal to $1/(q_{\mathrm{D}}/q_{\mathrm{ref}})$ and is called the sputtering-rate correction factor.

NOTE 1 The inverse emission yield is related to the emission yield, $\Re_{i\lambda}$, by using Formula (A.3):

$$R_{i\lambda} = 1/(q_{\mathrm{ref}} \times \Re_{i\lambda}) \tag{A.3}$$

where the emission yield is defined as Formula (A.4):

$$\Re_{i\lambda} \equiv \left(I_{i\lambda} - I_{\mathrm{B}\lambda}\right) \Big/ \left(w_{i\mathrm{D}} \times q_{\mathrm{D}}\right) \tag{A.4}$$

$I_{\mathrm{B}\lambda}$ being the spectral background intensity at wavelength λ.

NOTE 2 The two spectral background terms are related by Formula (A.5):

$$B_{\lambda \mathrm{rel}} = \left(q_{\mathrm{ref}} / q_{\mathrm{D}}\right) \times B_\lambda \tag{A.5}$$

These formulae can conveniently be modified to non-linear calibration curves, for example by incorporating second-order and higher-order terms. To illustrate such non-linear calibration curves, Formulae (A.1) and (A.2) can be expressed, with such second-order terms, as shown in Formulae (A.6) and (A.7), respectively:

$$w_{i\mathrm{D}} \times \left(q_{\mathrm{D}} / q_{\mathrm{ref}}\right) = R_{i\lambda} \times I_{i\lambda} + e_{i\lambda} \times I_{i\lambda}^2 - B_\lambda \tag{A.6}$$

and

$$w_{i\mathrm{D}} = R_{i\lambda} \times I_{i\lambda} \times \left(q_{\mathrm{ref}} / q_{\mathrm{D}}\right) + e_{i\lambda} \times I_{i\lambda}^2 \times \left(q_{\mathrm{ref}} / q_{\mathrm{D}}\right) - B_{\lambda \mathrm{rel}} \tag{A.7}$$

where $e_{i\lambda}$ is a constant describing the degree of non-linearity.

The actual calibration constants shall be obtained by regression analysis of the calibration data using a least-squares-fit algorithm.

The parameter q_{ref} is normally selected as the sputtering rate per unit area of some frequently used base material for calibration standards, e.g. low-alloy steel. This has the effect that, for several steel-based calibration specimens, the relative sputtering rates and the sputtering rate correction factors are both close to unity and insensitive to the plasma conditions.

The spectral background terms in Formulae (A.1) and (A.2) are not true constants, but are more or less matrix-dependent. In practical work, it is always advisable to select the lowest measured intensity as the fixed background for each spectral line.

All commercially available instruments manufactured today have provisions for subtraction of additional background signals from those of other analyte elements (line interference corrections). Where applicable, such corrections should be implemented.

A.4 Calculation of calibration constants using absolute sputtering rates

Calibration is conducted using Formula (A.8) or Formula (A.9):

$$w_{i\mathrm{D}} \times q'_{\mathrm{D}} = R'_{i\lambda} \times I_{i\lambda} - B'_{\lambda} \tag{A.8}$$

or

$$w_{i\mathrm{D}} = R'_{i\lambda} \times I_{i\lambda} \,/\, q'_{\mathrm{D}} - B'_{\lambda\mathrm{rel}} \tag{A.9}$$

where

$w_{i\mathrm{D}}$	is the mass fraction of element i in specimen D;
q'_{D}	is the sputtering rate, expressed as the mass loss rate, of specimen D;
$R'_{i\lambda}$	is the inverse emission yield of element i at spectral line λ (see also Note 1);
$I_{i\lambda}$	is the emission intensity of element i at spectral line λ;
B'_{λ}	is a spectral background term at wavelength λ which may be treated as a constant or as a more complex function, expressed as a mass fraction multiplied by the specimen sputtering rate, provided by the manufacturer;
$B'_{\lambda\mathrm{rel}}$	is a different but related spectral background term at wavelength λ which is expressed, in Formula (A.9), as a mass fraction, is often referred to as the "background equivalent concentration" and may be treated as a constant or as a more complex function provided by the instrument manufacturer (see also Note 2).

NOTE 1 The inverse emission yield is related to the emission yield, $\mathfrak{R}'_{i\lambda}$, by using Formula (A.10):

$$R'_{i\lambda} = 1 \,/\, \mathfrak{R}'_{i\lambda} \tag{A.10}$$

where the emission yield is defined as Formula (A.11):

$$\mathfrak{R}'_{i\lambda} \equiv \left(I_{i\lambda} - I_{\mathrm{B}\lambda}\right) / \left(w_{i\mathrm{D}} \times q'_{\mathrm{D}}\right) \tag{A.11}$$

$I_{\mathrm{B}\lambda}$ being the spectral background intensity at wavelength λ.

NOTE 2 The two spectral background terms are related as shown in Formula (A.12):

$$B'_{\lambda\mathrm{rel}} = B'_{\lambda} \big/ q'_{\mathrm{D}} \tag{A.12}$$

These formulae can conveniently be modified to give non-linear calibration curves, for example, by incorporating second-order and higher-order terms. To illustrate such non-linear calibration curves, Formulae (A.8) and (A.9) can be expressed, with such second-order terms, as shown in Formulae (A.13) and (A.14), respectively:

$$w_{i\,\mathrm{D}} \times q'_{\mathrm{D}} = R'_{i\lambda} \times I_{i\lambda} + e'_{i\lambda} \times I^2_{i\lambda} - B'_{i\lambda} \tag{A.13}$$

and

$$w_{i\,\mathrm{D}} = R'_{i\lambda} \times I_{i\lambda} \big/ q'_{\mathrm{D}} + e'_{i\lambda} \times I^2_{i\lambda} \big/ q'_{\mathrm{D}} - B'_{\lambda\mathrm{rel}} \tag{A.14}$$

where $e'_{i\lambda}$ is a factor describing the degree of non-linearity.

The actual calibration constants shall be obtained by regression analysis of the calibration data using a least-squares-fit algorithm.

The spectral background terms in Formulae (A.8) and (A.9) are not true constants, but are more or less matrix-dependent. In practical work, it is always advisable to select the lowest measured intensity as the fixed background for each spectral line.

All commercially available instruments manufactured today have provisions for subtraction of additional background signals from those of other analyte elements (line interference corrections). Where applicable, such corrections should be implemented.

A.5 Correction of elemental intensities and sputtered mass for variations in discharge parameters

A.5.1 General

Most commercial instruments have provisions for correcting the measured elemental intensities and sputtered mass for deviations from the source discharge parameter settings used in the calibration. For thin oxide layers (<100 nm), it is recommended that such corrections be used, since the sputtering of very thin layers occurs at least partly in a short time interval when the discharge parameters have not stabilized. These corrective calculations exist in two forms as described below.

A.5.2 Correction of elemental intensities based on tabulated constants for discharge parameters

For each element, *i*, and spectral line, *λ*, in segment *j* of the depth profile, calculate the corrected intensity, $I'_{i\lambda}$, using Formula (A.15):

$$I'_{i\lambda} = \left(\frac{s_j}{s_0}\right)^{a_\lambda} \times f\left(U_j\right) \tag{A.15}$$

where

a_λ is a factor characteristic of spectral line λ;

$f(U_j)$ is the value in segment *j* of a polynomial function (of degree 1 to 3) of the voltage, *U*, characteristic of spectral line λ;

s_j is the current in segment *j*;

s_0 is the reference current given by the instrument manufacturer.

Tabulated values of the exponential constant, a_λ, and the polynomial coefficients for $f(U)$ are usually given by the manufacturer of the instrument.

The corrected intensity, $I'_{i\lambda}$, is then inserted in Formulae (A.8), (A.9), (A.13) and (A.14) instead of $I_{i\lambda}$.

NOTE The exponential constant, a_λ, and the polynomial coefficients for $f(U)$ are instrument-independent constants characteristic of each spectral line.

A.5.3 Voltage correction of the emission yield in the calibration function

Since the variations in voltage and current are interdependent expressions of the plasma impedance at constant pressure, a correction can be based on just one of these parameters if the source is operated at constant pressure. A method of correction of the emission yield for voltage in the calibration function is to introduce a voltage dependence in the inverse emission yield in accordance with Formula (A.16):

$$R''_{i\lambda} = 1 + r^U_{i\lambda}\left(U_\mathrm{D} - U_\mathrm{av}\right) \tag{A.16}$$

where

$r^U_{i\lambda}$ is a regression parameter in the calibration function;

U_D is the voltage recorded for calibration specimen D;

U_av is the average voltage recorded for the set of calibration specimens used.

This type of formula is known as a "multiplicative" correction, and it appears in the calibration function as a type of "inter-element" correction where the voltage is treated as an additional element.

Since this voltage correction is implemented in the calibration function, no further calculation step need to be added to those described below.

The requirements for implementing the voltage correction are that

a) the source be operated at constant pressure,

b) either the DC bias voltage or the applied voltage be measured during calibration and analysis, and

c) a sufficient number of calibration specimens giving substantial variation in the operating voltage be used for calibration.

NOTE The regression parameter, $r^U_{i\lambda}$, is only valid for a specific calibration (method) and cannot be transferred between instruments.

A.5.4 Correction of sputtering rate for variations in discharge parameters

If corrections for intensity variations are carried out in accordance with A.5.2, it is necessary to make an additional correction for variations in sputtering rate due to the variations in the discharge parameters. For each segment, *j*, of the depth profile, calculate a corrected sputtering rate, q'_ref, of the reference specimen in accordance with Formula (A.17):

$$q'_\mathrm{ref} = \frac{s_j}{s_\mathrm{cal}}\left(\frac{U_j - U_0}{U_\mathrm{cal} - U_0}\right) \tag{A.17}$$

where

s_j is the current in segment j;

s_{cal} is the current used for the calibration of the method;

U_j is the voltage in segment j;

U_{cal} is the voltage used for the calibration of the method;

U_0 is the threshold voltage for sputtering.

The corrected sputtering rate of the reference specimen, q'_{ref}, is then inserted into Formulae (A.20) and (A.22) below instead of q_{ref}.

A.6 Correction of emission yields due to the influence of hydrogen

A.6.1 General

If present in sufficient quantity in the glow-discharge plasma, hydrogen has a strong influence on the emission yields of several spectral lines of analyte atoms. This will affect the measured intensities of these spectral lines. For thin oxide layers (<100 nm), it is recommended that this effect be corrected for, since several oxide types contain hydrogen. Additionally, other compounds containing hydrogen (water, hydrocarbons) are released from the interior walls of the glow-discharge source when the plasma ignites. These corrective calculations exist in two forms as described below.

A.6.2 Correction of elemental intensities based on reference hydrogen intensity and tabulated constants

For each spectral line, λ, of element i in segment j of the depth profile, calculate the corrected intensity, $I''_{i\lambda}$, using the equation

$$I''_{i\lambda} = I'_{i\lambda} \exp\left(b_\lambda \frac{I_{\mathrm{H}}}{I_{\mathrm{Href}}} \right) \tag{A.18}$$

where

b_λ is a constant describing the influence of hydrogen on the intensity of spectral line λ;

I_{H} is the observed hydrogen emission intensity;

I_{Href} is the hydrogen emission intensity from a reference material, e.g. a TiH_2 layer or a specific type of polymer.

The corrected intensity, $I''_{i\lambda}$, is then inserted instead of $I_{i\lambda}$ or $I'_{i\lambda}$ in the calculation of mass fractions and sputtered mass as described in A.6 to A.7.

NOTE The constant b_λ is an instrument-independent number characteristic of each spectral line. However, it also depends on the reference intensity, I_{Href}. This means that transferring constants between instruments requires use of the same reference material for measuring I_{Href} on both instruments.

A.6.3 Hydrogen correction of the emission yield in the calibration function

A multiplicative correction of the emission yield for hydrogen is inserted in the calibration function in accordance with Formula (A.19):

$$R''_{i\lambda} = r^{\mathrm{H}}_{i\lambda} \left(1 + I_{\mathrm{HD}}\right) \tag{A.19}$$

where

$r_{i\lambda}^{\mathrm{H}}$ is a regression parameter describing the influence of hydrogen on spectral line λ;

I_{HD} is the hydrogen intensity recorded for calibration specimen D.

Since this correction is implemented in the calibration function, no further calculation step need be added to those described below.

The requirements for implementing this hydrogen correction are that

a) the set of calibration specimens shall include at least one specimen with substantial hydrogen content, and

b) regression parameters, $r_{i\lambda}^{\mathrm{H}}$, can only be determined for elements present in substantial content in the hydrogen-rich specimens.

NOTE The regression parameter, $r_{i\lambda}^{\mathrm{H}}$, is only valid for a specific calibration (method) and cannot be transferred between instruments.

A.7 Calculation of mass fractions and sputtered mass using relative sputtering rates

A.7.1 General

The calculation of elemental mass fractions and sputtered mass can proceed in accordance with various different sets of algorithms described below, depending on the calibration function used. The final results are equivalent, however.

A.7.2 Calculation based on the relative elemental sputtering rate

If a calibration function based on Formula (A.1) was used for calibration, carry out the following calculation steps.

For each segment, j, of the depth profile, calculate from the calibration function the quantity $[w_{i\mathrm{D}} \times (q_{\mathrm{D}}/q_{\mathrm{ref}})]_j$ for each element, i, of specimen D. This quantity is called the “relative elemental sputtering rate”.

Provided that the sum of all the elements determined constitutes more than 98 % of the material analysed, calculate the relative sputtering rate, $(q_{\mathrm{D}}/q_{\mathrm{ref}})_j$, of segment j of the depth profile of specimen D using Formula (A.20):

$$\left(q_{\mathrm{D}}/q_{\mathrm{ref}}\right)_j = \sum_i \left[w_{i\,\mathrm{D}} \times \left(q_{\mathrm{D}}/q_{\mathrm{ref}}\right)\right]_j \Big/ 100 \qquad \text{(A.20)}$$

The mass fraction, $w_{i\mathrm{D}j}$, of element i in segment j of specimen D is given by Formula (A.21):

$$w_{i\mathrm{D}j} = \left[w_{i\mathrm{D}} \times \left(q_{\mathrm{D}}/q_{\mathrm{ref}}\right)\right]_j \Big/ \left(q_{\mathrm{D}}/q_{\mathrm{ref}}\right)_j \qquad \text{(A.21)}$$

where $w_{i\mathrm{D}j}$ is expressed in per cent.

The total sputtered mass per unit area, $m_{j\mathrm{tot}}$, in segment j and in the corresponding time increment, Δt_j, is given by Formula (A.22):

$$m_{j\mathrm{tot}} = q_{\mathrm{ref}} \times \left(q_{\mathrm{D}} / q_{\mathrm{ref}}\right)_j \times \Delta t_j \qquad \text{(A.22)}$$

A.7.3 Calculation based on the mass fractions of the elements

If a calibration function based on Formula (A.2) was used for calibration, carry out the following calculation steps.

Provided that the sum of all the elements determined constitutes >98 % of the material analysed, the mass fraction, $w_{i\mathrm{D}j}$, of element i in segment j of specimen D, expressed in per cent, is given by Formula (A.23):

$$w_{i\,\mathrm{D}j} = \frac{\left(k_{i\lambda} \times I_{i\lambda} - B_{\lambda\mathrm{rel}}\right)_j}{\sum\limits_i \left(k_{i\lambda} \times I_{i\lambda} - B_{\lambda\mathrm{rel}}\right)_j} \times 100 \tag{A.23}$$

where $k_{i\lambda}$ is equal to $R_{i\lambda} \times (q_{\mathrm{ref}}/q_{\mathrm{D}})$.

NOTE Formula (A.23) incorporates a normalization of the sum of all the mass fractions to 100 %.

If non-linear calibration curves are used, replace the linear functions shown in Formula (A.23) by the corresponding non-linear functions.

For each segment, j, of the depth profile of specimen D, calculate the sputtering rate per unit area, $q_{\mathrm{D}j}$, using Formula (A.24):

$$q_{\mathrm{D}j} = q_{\mathrm{ref}} \times \sum_i \left(k_{i\lambda} \times I_{i\lambda} - B_{\lambda\mathrm{rel}}\right) / \, 100 \tag{A.24}$$

For each segment, j, and corresponding time increment, Δt_j, of the depth profile of specimen D, the sputtered mass per unit area, $m_{i\mathrm{D}j}$, of element i is given by Formula (A.25):

$$m_{i\,\mathrm{D}j} = q_{\mathrm{D}j} \times w_{i\,\mathrm{D}j} \times \Delta t_j \; / \; 100 \tag{A.25}$$

The total sputtered mass per unit area, $m_{j\mathrm{tot}}$, in segment j is given by Formula (A.26):

$$m_{j\mathrm{tot}} = \sum_i m_{i\,\mathrm{D}j} \tag{A.26}$$

A.8 Calculation of mass fractions and sputtered mass using absolute sputtering rates

A.8.1 General

The calculation of elemental mass fractions and sputtered mass can proceed in accordance with various different sets of algorithms described below, depending on the calibration function used. The final results are equivalent, however.

A.8.2 Calculation based on elemental sputtering rate

If a calibration function based on Formula (A.8) was used for calibration, carry out the following calculation steps.

For each segment, j, of the depth profile of specimen D, calculate from the calibration function the quantity $\left(w_{i\,\mathrm{D}} \times q'_{\mathrm{D}}\right)_j$ for each element, i. This quantity is the elemental sputtering rate.

Provided that the sum of all the elements determined constitutes >98 % of the material analysed, calculate the sputtering rate, $q'_{\mathrm{D}j}$, of segment *j* of the depth profile of specimen D using Formula (A.27):

$$q'_{\mathrm{D}j} = \sum_i \left(w_{i\,\mathrm{D}} \times q'_{\mathrm{D}} \right)_j \Big/ 100 \tag{A.27}$$

The mass fraction, $w_{i\mathrm{D}j}$, of element *i* in segment *j* of specimen D is given by Formula (A.28):

$$w_{i\,\mathrm{D}j} = \left(w_{i\,\mathrm{D}} \times q'_{\mathrm{D}} \right)_j \Big/ q'_{\mathrm{D}j} \tag{A.28}$$

where $w_{i\mathrm{D}j}$ is expressed in per cent.

The total sputtered mass per unit area, $m_{j\mathrm{tot}}$, in segment *j* and in the corresponding time increment, Δt_j, is given by Formula (A.29):

$$m_{j\mathrm{tot}} = q'_{\mathrm{D}j} \times \Delta t_j \Big/ A_{\mathrm{D}} \tag{A.29}$$

where A_{D} is the area of the crater on specimen D.

A.8.3 Calculation based on mass fractions of the elements

If a calibration function based on Formula (A.9) was used for calibration, carry out the following calculation steps.

Provided that the sum of all the elements determined constitutes >98 % of the material analysed, calculate the mass fraction, $w_{i\mathrm{D}j}$, of element *i* in segment *j* of specimen D, expressed as a mass fraction in per cent, using Formula (A.30):

$$w_{i\,\mathrm{D}j} = \frac{\left(k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda} \right)_j}{\sum_i \left(k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda} \right)_j} \times 100 \tag{A.30}$$

where $k'_{i\lambda}$ is equal to $R'_{i\lambda} \big/ q'_{\mathrm{D}}$.

NOTE Formula (A.30) incorporates a normalization of the sum of all the mass fractions to 100 %.

If non-linear calibration curves are used, replace the linear functions shown in Formula (A.30) by the corresponding non-linear functions.

For each segment, *j*, of the depth profile, calculate the sputtering rate, $q'_{\mathrm{D}j}$, using Formula (A.31):

$$q'_{\mathrm{D}j} = \sum_i \left(k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda} \right) / 100 \tag{A.31}$$

For each segment, *j*, and corresponding time increment, Δt_j, of the depth profile, the sputtered mass, $m_{i\mathrm{D}j}$, of element *i* is given by Formula (A.32):

$$m_{i\,\mathrm{D}j} = q'_{\mathrm{D}j} \times w_{i\,\mathrm{D}j} \times \Delta t_j \;/\; 100 \tag{A.32}$$

The total sputtered mass per unit area, m_j, in segment *j* is given by Formula (A.33):

$$m_j = \sum_i m_{i\,\mathrm{D}j} \;/\; A_{\mathrm{D}} \tag{A.33}$$

A.9 Calculation of sputtered depth

A.9.1 General

The analytical method described in this document determines the sputtered mass and mass fractions of each element. To determine the sputtered depth, the density of the sputtered material has to be known. For the materials considered here, it can be estimated from the elemental composition and the densities of the pure elements.

There are two existing methods for calculating the sputtered depth, either of which can be utilized for the purposes of this analytical method.

A.9.2 Calculation based on constant atomic volume

For each segment, j, of the depth profile of specimen D, calculate the density, ρ_j, using Formula (A.34):

$$\rho_j = 100 / \sum_i \frac{w_{i\,\mathrm{D}j}}{\rho_i} \tag{A.34}$$

where ρ_i is the density of the pure element i.

For each segment, j, of the depth profile, calculate the thickness, z_j, of that segment using Formula (A.35):

$$z_j = \frac{m_{j\mathrm{tot}}}{\rho_j \times A_\mathrm{D}} \tag{A.35}$$

The total depth is determined by summing z_j over j using Formula (A.35). Though not strictly necessary, it is interesting to also calculate the sputtering rate per unit area in segment j by dividing $m_{j\mathrm{tot}}$ by Δt_j.

A.9.3 Calculation based on averaged density

For each segment, j, of the depth profile of specimen D, calculate the atomic fraction, A_{ij}, of each element, i, using Formula (A.36):

$$A_{ij} = \frac{\left(w_{i\,\mathrm{D}j} / W_i\right)}{\sum_i \left(w_{i\,\mathrm{D}j} / W_i\right)} \tag{A.36}$$

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 Formula (A.37):

$$\rho_j = \sum_i A_{ij} \times \rho_i \tag{A.37}$$

For each segment, j, of the depth profile, calculate the thickness, z_j, using Formula (A.35). The total depth is determined by summing z_j over the range of values of j that are of interest.

Annex B
(informative)

Suggestions concerning suitable spectral lines

Table B.1 — Suggested spectral lines for determination of given elements

Element	Wavelength (nm)	Estimated useful mass fraction range in %	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
Si	212,41	Not determined	
Si	251,61	Not determined	
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
Mg	383,83	0,001 to 100	

[a] Use non-linear calibration curve.

Annex C
(informative)

Determination of coating mass per unit area (coating areic mass)

C.1 General

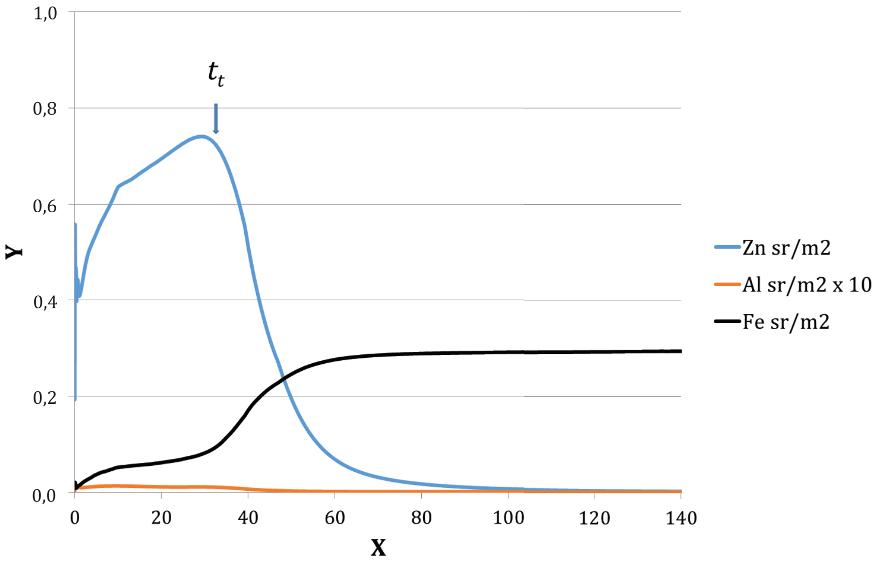
Calculation of the coating areic mass for a particular element can proceed by integrating the area under the depth profile for that element within the depth (or time) domain taken to represent the coating, an option available in the software of all commercial GD-OES instruments. How this integration is carried out can be understood from the quantitative depth profile expressed in ordinate units of $g/m^2/s$ and abscissa units of sec, available as an option for graphical presentation in the software of some commercial GD-OES instruments, see Figure C.1. The integrated areic mass of a specific element is obtained by summing the contributions from each time (depth) segment within the domain taken to represent the coating. Calculation of the total areic mass of a coating can then be accomplished by summing the coating areic masses for the individual elements. A key issue in these calculations is the determination of the domain that represents the coating. This is particularly true when a given element is present at significant mass fractions in both the coating and the substrate, e.g. a ZnFe coating on a steel substrate or an AlSi coating on an aluminium substrate. Due to the limited depth resolution it is impossible to directly separate the contributions from the coating and substrate respectively in the interface region from the elemental depth profile of that element. It is therefore necessary to make an indirect determination based on the depth profile of another major element in the coating. For such cases, the following two methods are recommended.

C.2 Method 1

First, consider an element that is present at a higher mass fraction in the substrate than in the coating. The approach for such an element is most easily explained by means of the galvanneal (ZnFe) coating example in Figure C.1 (see also Figure 2 in the main text). In this example, Fe is the element of interest. Time t_t or the corresponding depth d_d (when Fe in the base metal begins to appear) is defined as the time (or depth) at which the ordinate value for the major element in the coating (Zn in this case) falls to 95 % of its maximum or plateau-edge value. The time t_t or depth d_d can be determined from any of the three graphical presentations of the depth profile in Figure C.1. After time t_t, the Fe in the coating is assumed to decrease and reach zero in relation to the Zn profile, i.e. the Fe mass fraction of the coating material remains constant after time t_t (beyond depth d_d) . Therefore, the Fe areic mass within the transition zone is equal to the Zn areic mass between d_d and the integration end point L, multiplied by an adjustment factor equal to the ratio of the Fe to Zn ordinate values at d_d (t_t). The integration end point at depth D is defined as the Zn 50 % point plus three times the difference between depth d_d and the Zn 50 % point. At point D, the remaining Zn under the depth profile is assumed to be negligible. The total Fe areic mass is then the sum of the Fe areic mass within the transition zone and the Fe areic mass from time zero to t_t; see Figure C.2.

NOTE An alternative definition of t_t or d_d is possible, whenever there are monitored elements that are absent in the coating, but present in the substrate. In such a case, t_t may be defined as the time at which those elements are first detected. Nb, Mo, Mn, Cu and Co are examples of possible monitored elements.

In the case of coating elements that are present at higher mass fractions in the coating than in the substrate, the coating mass per unit area is taken to be the integral from time zero to the integration end point *L*.

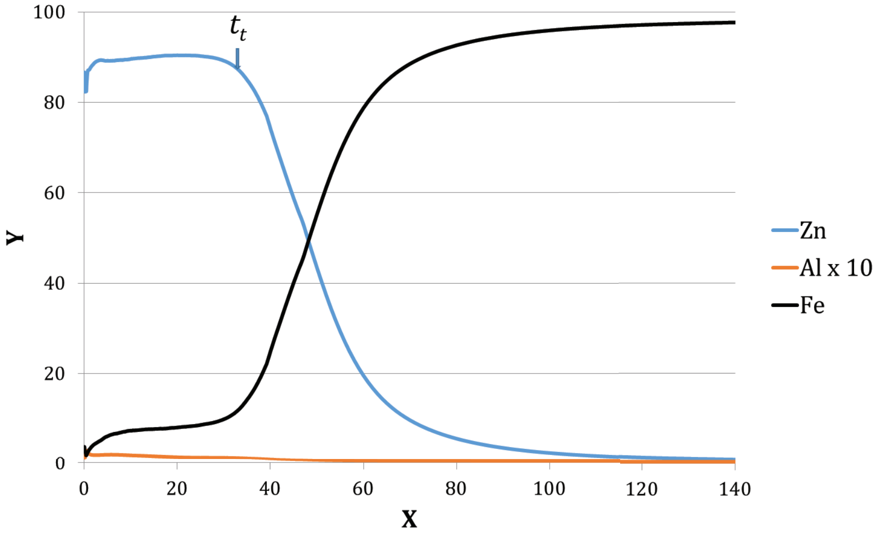


Key

X time (s)

Y elemental aeric sputtering rate (g/s/m^2)

t_t 95 % of maximum Zn sputtering rate

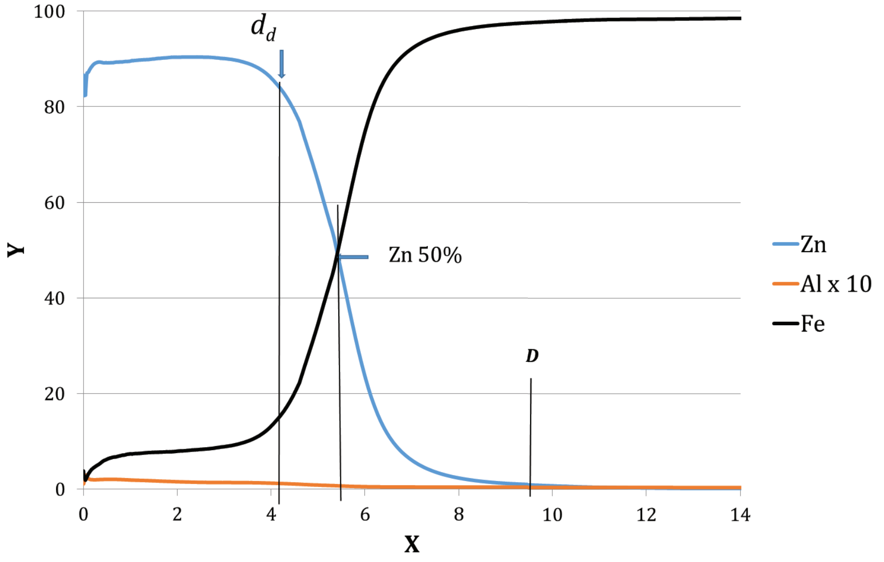


Key

X time (s)

Y elemental mass fraction (%)

t_t 95 % of Zn coating plateau value



Key

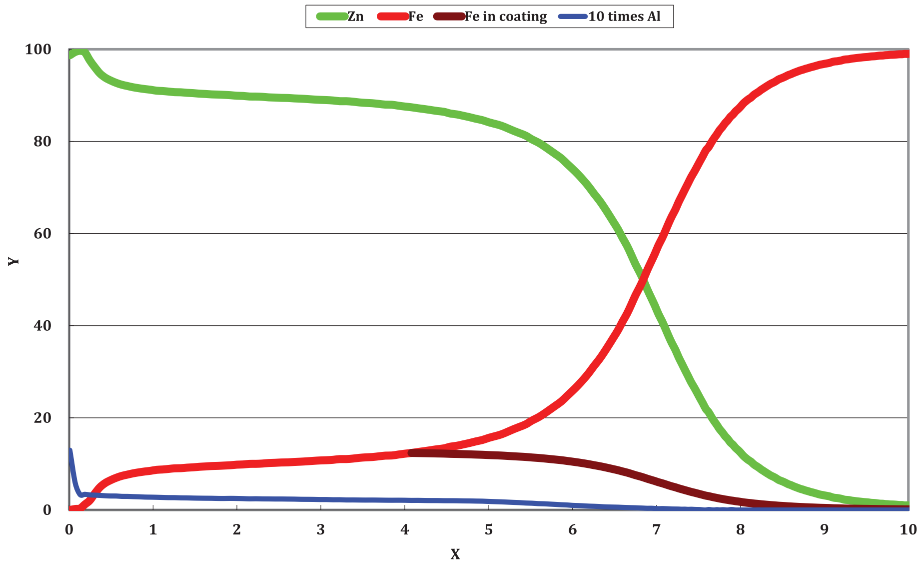
X depth (µm)

Y elemental mass fraction (%)

d_d 95% of Zn coating plateau value

D integration end point for Zn

Figure C.1 — Quantitative depth profiles for determination of the 95 % point of the Zn plateau value in a ZnFe galvanneal coating



Key

X depth (µm)

Y elemental mass fraction (%)

Figure C.2 — Quantitative depth profiles of a galvanneal ZnFe coating, with the Fe coating profile in the interface determined by method 1

C.2.1 Adjusting the Fe calibration

In order to obtain good agreement with wet chemical reference methods (in the case of ZnFe ISO 17925) within statistical limits, it is normally necessary to adjust the Fe calibration of the GD-OES method by the use of coated ZnFe RM's. There can be several reasons for discrepancies between GD-OES and wet chemical methods, the most likely are the following.

a) A slight difference between the Fe emission yield in the ZnFe and steels,since steels are normally used to calibrate for high Fe mass fractions (see 8.4).

b) The Fe mass fraction in the coating beyond depth d_d increases due to the presence of FeZn phases with higher Fe content, leading to an underestimation of the Fe areic mass in the range d_d to L.

In order to compensate for any discrepancies between GD-OES and reference methods, the following procedure is recommended.

a) Set up an appropriate GD-OES analytical method and calibrate according to Clause 8, using bulk calibration samples.

b) Analyse a few coated ZnFe RM's as unkowns, and apply method 1 to determine the Fe mass fraction in the coatings.

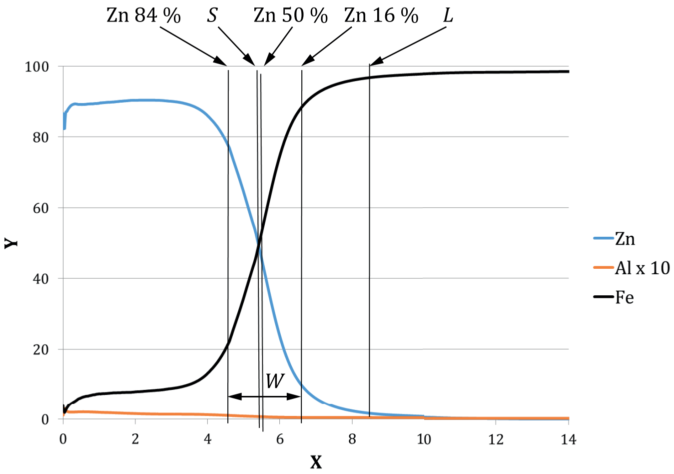
c) Calculate the ratio Fe (wet chemical)/Fe (GD-OES) for all ZnFe RM's; then, calculate the average ratio.

d) Multiply the slope of the Fe calibration function with the average ratio from step 3. How this change can be accomplished in an analytical method depends on the software of the particular instrument used, more detailed instructions can therefore not be given here.

e) Repeat step 2 with the adjusted Fe calibration. Verify that satisfactory agreement with the wet chemical data is obtained. If this is not the case, repeat steps 3 to 4 until satisfactory agreement is achieved.

C.3 Method 2

This procedure is based upon the compositional depth profile expressed in ordinate units of mass fraction and abscissa units of depth. As in method 1, a galvanneal (ZnFe) coating is used as an example. The following positions in the quantified depth profile are defined; see Figure C.3.



Key

X depth (µm)

Y analyte mass fraction (%)

W interface width

S depth at which mass fractions of Zn and Fe are equal

L depth corresponding to *S* plus *W*

Figure C.3 — Quantitative depth profile expressed as mass fraction vs. depth, illustrating method 2 for a ZnFe galvanneal coating

The first step is to find the depths at which the Zn mass fraction falls to 84 % and 16 % of the plateau Zn mass fraction in the coating. Designate these depths as Zn 84 % and Zn 16 %, respectively.

- Define the interface width *W* as the difference between Zn 16 % and Zn 84 %.
- Define depth *S* as the depth at which the mass fractions of Zn and Fe are equal.
- Define depth *L* as depth *S* plus the interface width *W*.
  - Calculate the (total) areic mass $Fe_{0\text{-}S}$ of Fe from depth zero to depth *S*.
  - Calculate the areic mass $Zn_{S\text{-}L}$ of Zn from depth *S* to depth *L*.

Based on the symmetry of the depth profiles of Zn and Fe, the Fe areic mass of the substrate up to the depth *S* is assumed to be proportional to the Zn areic mass beyond the depth *S*, mathematically expressed as Fe_{0-S} (substrate) = $\alpha_1 \times Zn_{S\text{-}L}$. The Fe areic mass from *S* to *L* in the coating is similarly assumed to be proportional to $Zn_{S\text{-}L}$; mathematically expressed as Fe_{S-L} (coating) = $\alpha_2 \times Zn_{S\text{-}L.}$ By combining these expressions, the total Fe areic mass of the coating $Fe_{0\text{-}L}$ (coating) is calculated according to Formula (C.1):

$$Fe_{0\text{-}L}\,(\text{coating}) = Fe_{0\text{-}S}\,(\text{total}) - \alpha \times Zn_{S\text{-}L} \tag{C.1}$$

Where α is an adjustment factor which has to be empirically determined for each application. For ZnFe coatings with an average Fe mass fraction close to 10 %, it has been found that α = 0,85 gives results in good agreement with wet chemical reference methods. However, the correct value for α varies and depends on several factors e.g. instrument type, glow-discharge source parameters and coating type.

Annex D
(informative)

Additional information on international cooperative tests

Table 1 and Table 2 were derived from the results of international analytical trials carried out in 2001 and 2002 on zinc and/or aluminium-base coating samples in three countries involving four laboratories.

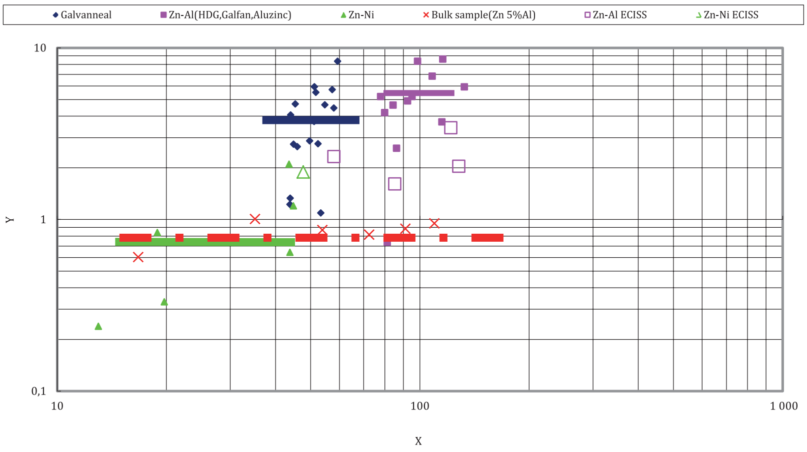
The results of the trials were reported in document ISO/TC 201/SC 8 N 38 revised (see 8 in Annex E) and N 55 (see 9 in Annex E).

The test samples used and results for coating areic mass and element contents obtained in international cooperative tests are listed in Table D.1.

The precision data are presented in graphical form in Figure D.1 and Figure D.2. They include data on bulk samples and results of inter-laboratory tests carried out at ECISS/TC 20.

Table D.1 — Test sample used and their found values

Samples		Coating areic mass g/m^2	Chemical composition (mass %)					
No.	**Kinds of coating**		**Zn**	**Fe**	**Al**	**Ni**	**Si**	**Pb**
3	Zn-Fe(Hot dip coating and annealing; Galvanneal)	57	89,1	10,23	0,210			
101	Zn-Fe(Hot dip coating and annealing; Galvanneal)	49,0	88,3	11,3	0,37			
102	Zn-Fe(Hot dip coating and annealing; Galvanneal)	50,7	89,5	10,05	0,38			
103	Zn-Fe(Hot dip coating and annealing; Galvanneal)	49,7	90,6	9,0	0,39			
104	Zn-Fe(Hot dip coating and annealing; Galvanneal)	53,3	86,6	13,03	0,37			
4	Al-Zn (Hot dip coating)	91,4	42,6		54,9		1,29	
12	Zn-Ni(Electrolytic coating)	17,81	86,2			12,5		
201	Zn(Hot dip coating)	113	99,5		0,35			0,11
202	Zn-Ni(Electrolytic coating)	44	86,7			13,2		
203	Zn(Hot dip coating; Galfan)	110	94,9		5,1			
204	Al-Zn(Hot dip coating; Aluzinc)	81	45,4		53,2		1,9	

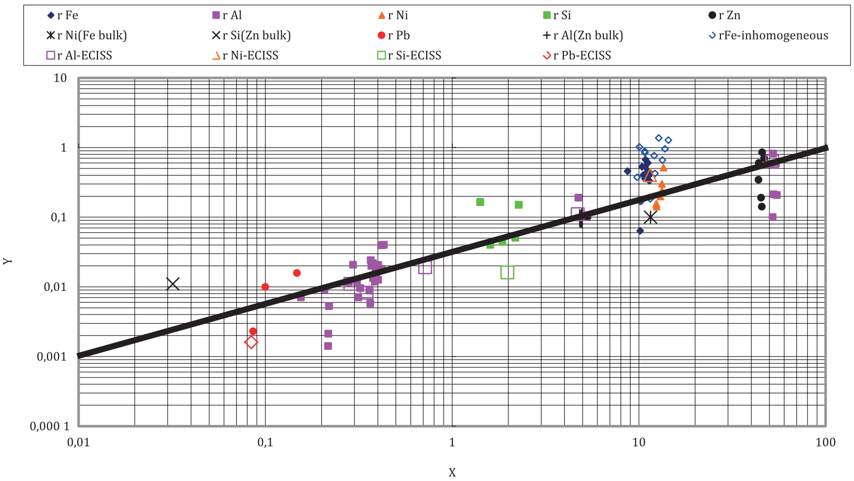


Key

X coating areic mass (g/m^2)

Y repeatability standard deviation (SDr) (g/m^2)

Figure D.1 — Relationship between coating areic mass and repeatability standard deviation (SD$_r$)



Key

X element content (mass %)

Y repeatability standard deviation (SDr) (mass %)

Figure D.2 — Logarithmic relationship between element contents and repeatability standard deviation

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