INTERNATIONAL STANDARD

ISO 16962

First edition
2005-10-01

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

Analyse chimique des surfaces — Analyse des revêtements métalliques à base de zinc et/ou d'aluminium par spectrométrie d'émission optique à décharge luminescente

Reference number
ISO 16962:2005(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

STANDARDSISO.COM : Click to view the full PDF of ISO 16962:2005

© ISO 2005

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16962 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

It is based on the results from project SMT-CT96-2080, funded by the EC Industrial and Materials Technologies Programme. The project was initiated by ECISS/TC 20.

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

1 Scope

This International Standard 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 10 mass %;

lead contents between 0,005 mass % and 2 mass %;

antimony contents between 0,005 mass % and 2 mass %.

2 Normative references

The following referenced documents are indispensable for the application 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 14707, *Surface chemical analysis — Glow discharge optical emission spectrometry (GD-OES) — Introduction to use*

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 Principle

The analytical method described here involves the following processes:

a) Cathodic sputtering of the surface coating in a direct current or radio frequency glow discharge device.

b) Excitation of the analyte atoms in the plasma formed in the glow discharge device.

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

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

4 Apparatus

4.1 Glow discharge optical emission spectrometer

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, incorporating suitable spectral lines for the analyte elements (see Annex B for suggested lines).

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

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

4.2 Minimum performance requirements

4.2.1 General

It is desirable for the instrument to conform to the performance specifications given in 4.2.2 and 4.2.3, and evaluated in 6.2.7.

NOTE Setting up for analysis commonly requires an iterative approach to the adjustment of the various experimental parameters.

4.2.2 Minimum repeatability

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

Perform 10 emission intensity measurements on a homogeneous bulk sample with an analyte content exceeding 1 mass %. The glow discharge conditions shall be those selected for the actual 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 sample. 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.

4.2.3 Detection limit

4.2.3.1 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 Zn/Al-based alloys considered here. For the purposes of this International Standard, the detection limit for each analyte will be acceptable if it is equal to or less than one-fifth of the lowest mass fraction expected in the coating or one-fifth of the lower end of the range of mass fractions quoted in Clause 1 of this International Standard, whichever is greater.

4.2.3.2 SNR method

The first method is often called the SNR (signal-to-noise ratio) method. In order to determine the detection limit for a given analyte, the following steps shall be performed:

1) Select a bulk sample to be used as a blank. The composition of the sample shall be similar to that of the coatings to be analysed in terms of the elemental composition of the matrix. Further, it shall be known to contain less than 0,1 µg/g of the analyte.

2) Perform ten replicate burns on the blank. For each burn, acquire the emission intensity at the analytical wavelength for 10 s. These are the background emission intensity measurements. The glow discharge conditions used shall be the same as those that will be used in the analysis of the coated samples. 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.

3) Compute the detection limit, expressed as a mass fraction, using the following equation:

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

where

DL is the detection limit;

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

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

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

4.2.3.3 SBR-RSDB method

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

1) Select a bulk sample that has a matrix composition that is similar to that of the coatings to be analysed, and for which the mass fraction of the analyte is greater than 0,1 % and known. If an analytical transition that is prone to self-absorption (see 6.1) is to be used, then the mass fraction of the analyte shall not exceed 1 %.

2) Perform three replicate burns on the chosen sample. 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 samples. For each measurement, the sample 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 sample for each individual burn. Average the three replicate emission intensities.

3) Select a peak-free region of the emission spectrum within 0,2 nm of the analytical peak. Perform ten replicate burns on the chosen sample. 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 an unsputtered area of the surface of the sample for each individual burn. Compute the average and relative standard deviation of the 10 replicate measurements.

4) Calculate the detection limit using the following equation:

$$\mathrm{DL} = \frac{3 \times (\mathrm{MF} \times \mathrm{RSDB}/100)}{(S - B)/B} \tag{2}$$

where

DL is the detection limit;

MF is the mass fraction of the analyte in the sample;

RSDB is the relative standard deviation of the background from step 3, expressed as a percentage;

B is the average background intensity from step 3;

S is the average peak intensity from step 2.

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

5 Sampling

As appropriate, carry out sampling in accordance with ISO 14284 and/or relevant national/international standards. If such standards are unavailable, follow the instructions from the manufacturer of the coated material or another appropriate procedure. Avoid the edges of coated strips. The size of the test samples shall be suitable for the glow discharge source used. Typically, round or rectangular samples with sizes (diameter, width and/or length) of 20 mm to 100 mm are suitable.

Rinse the surface of the sample with an appropriate solvent (high-purity acetone or ethanol) 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. After wiping, flush the surface with solvent and dry as described above.

6 Procedure

6.1 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 spectral interference from other elements present in the samples. In this type of application, where most of the analytes of interest are major elements in the samples, special attention shall be paid to the occurrence of self-absorption of certain highly sensitive spectral lines (so-called resonance lines). Self-absorption causes non-linear calibration curves at high analyte mass fraction levels, and strongly self-absorbed lines shall therefore be avoided for the determination of major elements. In Annex B, some suggestions concerning suitable spectral lines are given. Spectral lines other than those listed may be used, so long as they have favourable characteristics.

6.2 Optimizing the glow discharge spectrometer system settings

6.2.1 General

Follow the manufacturer's instructions or locally documented procedures for preparing the instrument for use. The source parameters shall be chosen to achieve three aims:

- adequate sputtering of the sample, to reduce the analysis time without over-heating the coatings;
- good crater shape, for good depth resolution;
- constant excitation conditions in calibration and analysis, for optimum accuracy.

There are often tradeoffs among the three specified aims.

In particular, check that the entrance slit to the spectrometer is correctly adjusted, following the procedure given by the instrument manufacturer. This ensures that the emission intensities are measured on the peaks of the spectral lines for optimum signal-to-background ratio. For further information, see ISO 14707.

6.2.2 Setting the discharge parameters of a dc source

6.2.2.1 General

Modern dc glow discharge spectrometers usually have provisions for complete control/measurement of the electrical parameters (current, voltage, power), allowing any two of these parameters to be locked to constant values by varying the pressure (active pressure regulation). Older spectrometers often lack an active pressure regulation system, but the pressure can still be adjusted manually to achieve the same result. The user shall adopt one of the following procedures.

6.2.2.2 Constant applied current and voltage

The two control parameters are applied current and voltage. Set the power supply for the glow discharge source to constant current/constant voltage operation. First set the current and voltage to typical values recommended by the manufacturer. If no recommended values are available, set the 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 about the optimum current is available, it is recommended that, to start with, a value somewhere in the middle of the recommended range is used.

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

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

Optimize the crater shape as described in 6.2.6, by adjusting the voltage. These conditions are then used during calibration and analysis.

6.2.2.3 Constant applied current and pressure

The two control parameters are applied current and pressure. Set the power supply for the glow discharge source to constant current operation. First set the current to a typical value recommended by the manufacturer. If no recommended values are available, set the current to a value in the range 5 mA to10 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 about the optimum current is available, it is recommended that, to start with, a value somewhere in the middle of the recommended range is used. Sputter a typical coated test sample, and adjust the pressure until a voltage of approximately 600 V is attained in the coating.

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

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

Optimize the crater shape as described in 6.2.6, by adjusting the pressure. Before sputtering a new sample type, make a test run in order to ensure that the voltage is not altered more than 5 % from the previously selected value. If this is the case, readjust the pressure until the correct value is attained. These conditions are then used during calibration and analysis.

Emission yields vary with the current, voltage and possibly the pressure (see Reference [4] in the Bibliography). It is therefore essential that these parameters be kept as closely as possible at the same levels during measurement of coated samples as during calibration. Since it is impossible in practice to maintain all three parameters constant for all samples, priority is given to maintaining current and voltage constant, utilizing the pressure as a variable parameter. There exists a method to correct for voltage and current variations by means of an empirically derived function (see Reference [4]) and this type of correction is often implemented in software based on the intensity normalization method in accordance with Equation (A.2) in Annex A. However, such corrections for voltage and current are not included in this standard method. If available in the spectrometer software, the user shall therefore ensure that the voltage-to-current corrections are disabled in order to implement the method correctly.

6.2.3 Setting the discharge parameters of an rf source

6.2.3.1 General

Currently, most rf sources are operated with constant applied power and constant pressure. Other modes also exist, such as constant applied voltage and pressure, and constant effective power and applied voltage. These modes are likely to become more common in the future. All rf operational modes are allowed in this International Standard provided they meet the three aims listed in 6.2.1. In the following, separate instructions are provided on how to set the parameters for the operational modes that are currently used regularly.

6.2.3.2 Constant applied power and pressure

The two control parameters are applied power and pressure. First set the applied power and adjust the source pressure to those suggested by the manufacturer. If recommended values are not available, set the applied power and pressure to somewhere in the middle of the ranges commonly used for depth profiling of metal samples. Measure the penetration rate (i.e. depth per unit time) on an iron or steel sample. Adjust 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 6.2.4.

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

Optimize the crater shape as described in 6.2.6, by adjusting the pressure.

Re-measure the penetration rate on the iron or steel sample and adjust the applied power if necessary to return to about 2 µm/min to 3 µm/min. Repeat the cycles 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 by the instrument. These conditions are then used during calibration and analysis.

6.2.3.3 Constant applied power and dc bias voltage

The two control parameters are applied power and dc bias voltage. First set the applied power and adjust the source pressure to attain a dc bias typical of those 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 ranges commonly used for depth profiling of metal samples. 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 sample. Adjust 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 6.2.4.

Adjust the discharge parameters as described in 6.2.5, adjusting first the applied power and if necessary the dc bias voltage.

Optimize the crater shape as described in 6.2.6, by adjusting the dc bias voltage.

Re-measure the penetration rate on the iron or steel sample and adjust the applied power if necessary to return to about 2 µm/min to 3 µm/min. Repeat the cycles of power and dc bias voltage adjustment until no significant change is noted in the penetration rate or 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 by the instrument. These conditions are then used during calibration and analysis.

6.2.3.4 Constant effective power and rf voltage

The two control parameters are effective power and rf voltage. Constant effective power is defined here as the applied power minus reflected power and the “blind power” measured with the sample in place but without plasma (vacuum conditions). The rf voltage is defined here as the RMS voltage at the coupling electrode.

Set the power supply for the glow discharge source to constant effective power/constant rf voltage operation. First set the power to typical values 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, for example. If no previous knowledge about the optimum power is available, it is recommended that, to start with, a value somewhere in the middle of the recommended range is used.

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

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

Optimize the crater shape as described in 6.2.6, by adjusting the rf voltage.

Re-measure the penetration rate on the iron or steel sample and adjust the applied power if necessary to return to about 2 µm/min to 3 µm/min. Repeat the cycles of power and dc bias voltage adjustment until no significant change is noted in the penetration rate or 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 by the instrument. These conditions are then used during calibration and analysis.

6.2.4 Setting the high voltage of the detectors

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

6.2.5 Adjusting the discharge parameters

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

6.2.6 Optimizing crater shape

Sputter one of the brass samples (see 6.3.2), or a Zn- and/or Al-based coating typical of the unknown samples, to a depth of about 10 µm to 20 µm (but still inside the coating if a coated sample is used) and measure the crater shape by means of a suitable profilometer device. Repeat this procedure on the brass or coating sample a few times using slightly different values of one of the control parameters. Select the conditions that gives an optimally flat-bottomed crater.

6.2.7 Preliminary performance test

Ensure that the selected operating parameters are adequate to meet the minimum performance requirements described in 4.2. If these minimum performance requirements are not satisfied, then additional adjustments to the operating parameters will be necessary.

6.3 Calibration

6.3.1 General

Calibration of the system consists of determining, for each analyte and spectral line, the analytical response curve as described in either Clause A.2 or Clause A.3 in Annex A. 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.

6.3.2 Calibration samples

6.3.2.1 General

Whenever possible, spectrometric calibration samples issued as CRMs (certified reference materials) shall 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. In particular, pure or nearly pure zinc samples are not recommended, due to difficulties in obtaining reproducible and stable sputtering rates in zinc. Furthermore, high-purity metals are not necessary in order to calibrate correctly for high mass fractions, but they are valuable for the determination of the spectral backgrounds. The following considerations are the most important in the selection of the calibration samples:

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

b) the samples shall be homogeneous.

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

6.3.2.2 Brass calibration samples

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

6.3.2.3 Zn-Al alloy samples

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

6.3.2.4 Iron or low-alloy steel samples

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

6.3.2.5 Stainless-steel samples

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

6.3.2.6 Nickel alloy samples

Select at least one nickel-based alloy sample with a nickel mass fraction higher than 70 % (an Ni mass fraction higher than the 20 % defined in Clause 1 is necessary due to the high sputtering rate of Zn-Ni alloys, the calibration points being defined by the product of sputtering rate and mass fraction).

6.3.2.7 Aluminium-silicon alloy samples

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

6.3.2.8 High-purity copper sample

Select a high-purity copper sample with analyte mass fractions of less than 0,001 %. This sample can be used as the zero point for all analytes except copper.

6.3.3 Validation samples and optional RMs for calibration

6.3.3.1 General

Validation (see 6.4) samples shall 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.

6.3.3.2 Electrolytically coated zinc-nickel RM

Prepare an electrolytically coated RM with a nickel mass fraction less than 20 %. Determine the coating mass per unit area and chemical composition of the coated RM by specified reference methods such as ISO 17925.

6.3.3.3 Electrolytically coated zinc RM

Prepare an electrolytically RM with a zinc mass fraction higher than 30 % and an iron mass fraction higher than 5 %. Determine the coating mass per unit area and chemical composition of the coated RM by specified reference methods such as ISO 17925.

6.3.3.4 Zinc-aluminium coated RM

Prepare a zinc-aluminium coated RM with a zinc mass fraction higher than 10 % and an aluminium mass fraction higher than 5 %. Determine the chemical composition of the coated RM by specified reference methods such as ISO 17925.

NOTE 1 A reference material (RM) is a 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, for the assessment of a measurement method or for assigning values to materials.

NOTE 2 A certified reference material (CRM) is a 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, each certified value being accompanied by an uncertainty at a stated level of confidence. A Standard Reference Material® (SRM®) is a CRM issued by the National Institute of Standards and Technology, Gaithersburg, MD, USA.

6.3.4 Determination of the sputtering rate of calibration samples

The term “sputtering rate” is understood here to be equivalent to the mass loss rate during sputtering in the glow discharge. The term “relative sputtering rate” is understood here to be the sputtering rate of the sample divided by the sputtering rate of a reference material sputtered under the same conditions. If the sputtered areas of the sample and the reference sample 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 (sputtering rates may also be available from the manufacturer):

a) If laboratory facilities are available, measure the density of each calibration sample. A suitable method for homogeneous samples is sample mass divided by sample volume where the sample volume is measured by immersion of the sample in water, using Archimedes' principle. Alternatively, the sample volume could be estimated from the sample dimensions, or the density calculated from the sample composition as described in Annex A [see Equation (A.29)]. The accuracy of the measured or calculated density shall be better than 5 %.

b) Prepare the sample surface in accordance with the instrument manufacturer's recommendations or another appropriate procedure.

c) Adjust the glow discharge parameters to those selected in 6.2.

d) Sputter the sample for a time estimated to result in a crater 20 µm to 40 µm deep, recording the total sputtering time.

e) Repeat d) several times if the sample surface area is sufficiently large, recording the total sputtering time for each crater.

f) 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.

g) 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 sputtered volume multiplied by the density of the sample;

    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.

h) 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 sample;

    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 sample (iron or low-alloy steel is recommended) and measure the average sputtering rate per unit area for this reference sample as described above for the calibration samples;

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 used in the depth calibration shall have an accuracy of better than 5 %.

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

6.3.5 Emission intensity measurements of calibration samples

The procedure for measuring the calibration samples is as follows:

a) Prepare the surfaces of the calibration samples 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 sample. However, wet grinding may be beneficial. Wet samples can be dried by thoroughly rinsing them with alcohol and then blowing the solvent away with a stream of inert gas, such as argon or nitrogen. Be careful not to touch the sample surface with the gas delivery tube.

b) Adjust the source parameter settings to those selected in 6.2. 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 units in which the intensities are given is of no importance. Commonly used units are counts per second (cps) or volts (V). Measure each sample at least two times and calculate the average value.

6.3.6 Calculation of calibration constants

Perform the calibration computations in accordance with the methods specified in either Clause A.2 or Clause A.3 in Annex A.

NOTE Depending on the type of source, the mode of operation and the calibration samples chosen, the calibration graphs for some elements may show a large separation between samples from different matrices. The separation typically occurs between two matrix groups: one group including low-alloy steel, stainless steel and brass, and a second group including aluminium and aluminium-zinc alloys. This separation has been noted in elemental calibration graphs where samples from both matrix groups are included. This separation is proof of a difference in emission yield, and has been shown to be well correlated to matrix-dependent variations in the glow discharge plasma. If some facility is provided by the manufacturer to minimize this effect, it should be used. Otherwise the solution is to choose, from each calibration curve, calibration samples which most resemble the samples to be analysed. This normally does not present any special difficulty. For zinc, for example, when analysing aluminium-zinc coated steel, the brass samples are excluded from the calibration graph.

6.4 Validation of the calibration

6.4.1 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 sample is analysed. A related procedure (verification) shall be used on a more routine basis to check for instrument drift over time, as described in 6.5.

Two validation procedures are included in the subclauses that follow. The first procedure (see 6.4.2) makes use of bulk reference materials, and the second (see 6.4.3) employs coated reference materials. Such coated reference materials are often difficult to obtain. As a result, the validation procedure described in 6.4.3 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 (see ISO 9000:2005, Subclause 3.8.5). Validation of the method is defined in ISO/IEC 17025:2005, Subclause 5.4.5. Validation of the calibration is analogous to it (cf. Note to 6.5).

6.4.2 Checking analytical accuracy using bulk reference materials

a) Select an appropriate number of bulk reference materials to be used for validation of the calibration, in accordance with 6.3.2.

b) Measure the emission intensities for these validation samples under the same glow discharge conditions and preburn and integration times as selected for calibration. At least three independent burns shall be placed on each sample, using a freshly prepared surface for each burn.

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

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

6.4.3 Checking analytical accuracy using coated reference materials

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

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

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

d) Follow the instrument manufacturer's instructions for calculating the relationship between intensity versus time (qualitative) and mass percent versus depth in µm (quantitative). Modern instrumental software will automatically calculate this relationship at the end of each analysis.

e) Calculate the coating mass in g/m^2. Coating mass per unit area can be calculated using theoretical or calculated densities. The difference between the assigned value and the calculated value shall not exceed ± 10 %.

f) Calculate the coating depth in µm. The difference between the value assigned to a reference material and the calculated value shall be ± 5 % or less. The difference between the value assigned to 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 the tolerances cited in item f) above, then the calibration constants are acceptable.

h) Calculate the average chemical composition, in mass percent, of the analytes present in the coating and substrate. The calibration constants are acceptable if the relative accuracy for the major elemental mass fractions (> 1 %) are ± 5 % or less in most cases.

i) If validation is not successful, repeat the calibration.

When the curves are properly adjusted, the accuracy of the mass fractions and the depth axis will be ensured.

6.5 Verification and drift correction

The analytical response of modern instrumentation may 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 samples 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 pieces (standardants) to be used for verification of the calibration.

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

c) Compute the average mass fractions of the analytes for each sample, 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 statistical disagreement is found, carry out a drift correction in accordance with the instrument manufacturer's instructions.

It is recommended that a verifier be analysed after drift correction to prove the accuracy of the calibration graph.

NOTE Verification is the confirmation, through the provision of objective evidence, that specified requirements have been fulfilled (see ISO 9000:2005, 3.8.4, and compare Note to 6.4.1).

6.6 Analysis of test samples

Analyse test samples in accordance with the procedure described in 6.1 and 6.2, using calibration graphs established in accordance with 6.3, 6.4 and 6.5.

7 Expression of results

7.1 Quantitative depth profile

Generate a quantitative depth profile, a typical example of which is shown in Figure 1.

7.2 Determination of total coating mass per unit area

The total coating mass per unit area, in g/m^2, for each element is calculated using the relevant algorithms given in Clause A.3 or Clause A.4 and the computing procedure given in Annex C. Integrate m_{iMj} in Equation (A.20) or (A.27) for a time interval corresponding to the coating depth. Conversion from the time to the depth and *vice versa* for integration is made using the algorithms in Clause A.5.

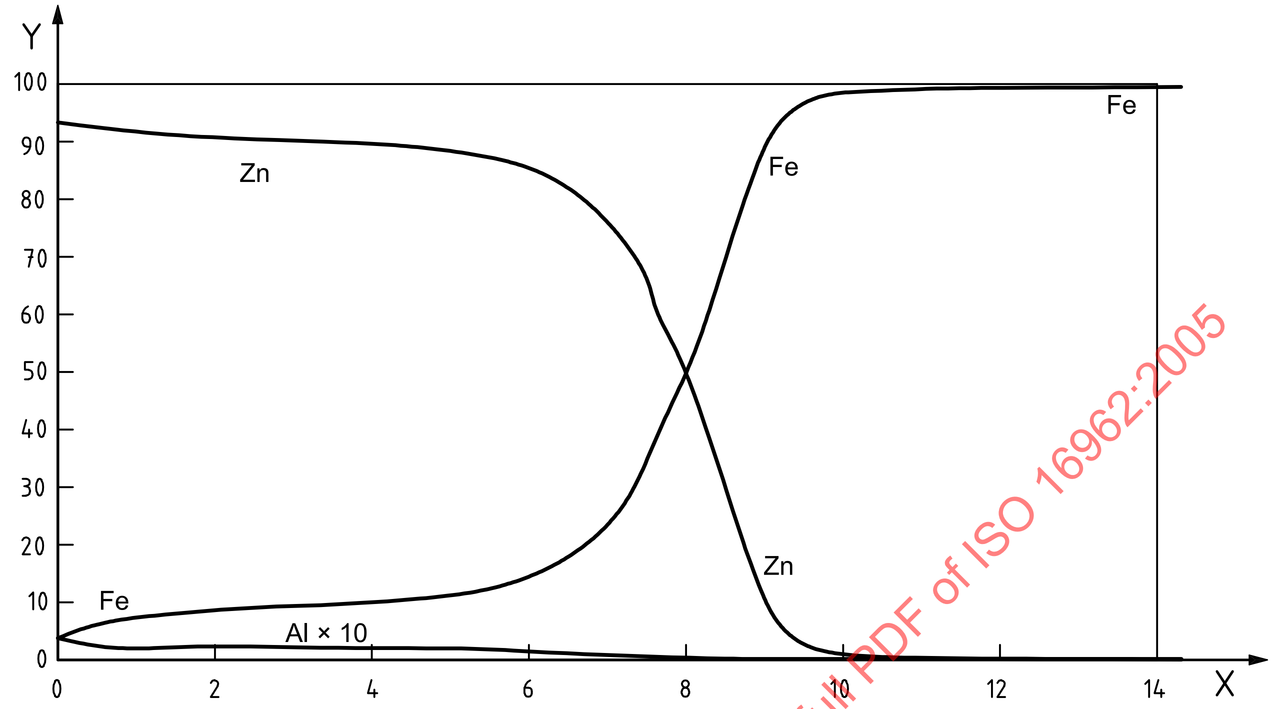
NOTE The integration is carried out on the depth profile of g/m^2/s versus time in seconds. However, this procedure may be hidden in the software of commercial instruments. In this case, the integration is carried out in accordance with C.3.2 in Annex C.

For the major elements, the following recommendations are given for the determination of the integration depth:

a) Define the coating thickness as the depth at which the mass fraction of the major element is reduced to 50 % of the maximum value in the coating. The maximum value is the highest mass fraction between start and Zn = 84 %.

b) Define the width of the interface region (which is equivalent to the practical depth resolution) as the difference between the depth at which the mass fractions of the major element in the coating is reduced to 84 % of the maximum value in the coating and the depth at which it is reduced to 16 % of its maximum value.

c) The integration depth is the sum of the coating thickness and the interface width.



Key

X depth, µm

Y analyte mass percent

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

7.3 Determination of average mass fractions

The average mass fraction of each element is computed by dividing the coating mass for that element by the sum of the coating masses for all the elements.

8 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 defined in ISO 5725-1, i.e. one operator, same apparatus, identical operating conditions, same calibration and a minimum period of time. The repeatability limit has been calculated in accordance with ISO 5725-6. The data obtained are summarized in Table 1 and Table 2. Graphical representations of the data are given in Annex D.

NOTE The precision obtained for hot-dip-coated steel is in practice governed mainly by the inhomogeneity of industrially produced samples, not by measurement capability.

Table 1 — Results for repeatability standard deviation and repeatability limit of coating mass per unit area

Values in g/m^2

Type of coating	Repeatability standard deviation s_r	Repeatability limit r (= 2,8s_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 (= 2,8s_r)
Less than 0,1	0,006	0,017
1	0,03	0,084
10	0,2	0,56
99	1	2,8

9 Test report

The test report shall include the following information:

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

b) the laboratory and the date of analysis;

c) the method used, by reference to this International Standard;

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

e) any unusual features noted during the determination;

f) details of any operation not specified in this International Standard, as well as any optional operation which may have influenced the results.

Annex A
(normative)

Calculation of calibration constants and quantitative evaluation of depth profiles

A.1 Symbols

A.1.1 Symbols used generally in this annex

a_{ij}	atomic fraction of element i in segment j
A_M	area of crater on sample M
c_{iM}	mass fraction of element i in sample M
c_{iMj}	mass fraction of element i in segment j of sample M
Δt_j	time increment in segment j
i	element
$I_{i\lambda}$	emission intensity of wavelength λ of element i
j	segment of depth profile
$M_{j\text{tot}}$	total sputtered mass per unit area in segment j
ρ_i	density of pure element i
ρ_j	density in segment j
w_i	atomic mass of element i
z_j	thickness of segment j

A.1.2 Symbols used in Clauses A.2 and A.4 concerned with relative sputtering rates

B_λ	spectral background term at wavelength λ, expressed in mass %
$B_{\lambda\text{rel}}$	related spectral background term at wavelength λ, expressed in mass %
b_λ	spectral background intensity at wavelength λ
$[c_{iM} \times (q_M/q_{\text{ref}})]_j$	relative elemental sputtering rate for element i in segment j
$k_{i\lambda}$	constant factor derived from inverse emission yield divided by relative sputtering rate
m_{iMj}	sputtered mass per unit area of element i in segment j of sample M
q_M	sputtering rate, expressed as mass loss rate per unit area of sample M

q_{Mj}	sputtering rate expressed as mass loss rate per unit area in segment j
q_M/q_{ref}	sputtering rate of sample M relative to reference sample
q_{ref}/q_M	sputtering rate correction factor for sample M relative to reference sample
$R_{i\lambda}$	inverse emission yield of element i at spectral line λ
$\mathfrak{R}_{i\lambda}$	emission yield of element i at spectral line λ
$s_{i\lambda}$	constant describing degree of non-linearity

A.1.3 Symbols used in Clauses A.3 and A.5 concerned with absolute sputtering rates

B'_λ	spectral background term at wavelength λ, expressed as mass % × g/time
$B'_{\lambda\mathrm{rel}}$	related spectral background term at wavelength λ, expressed as mass % × g/time
$(c_{iM} \times q'_M)_j$	elemental sputtering rate for element i in segment j
$K'_{i\lambda}$	constant factor derived from inverse emission yield divided by sputtering rate
M_{iMj}	sputtered mass of element i in segment j of sample M
Q'_M	sputtering rate or mass loss rate of sample M
Q'_{Mj}	sputtering rate or mass loss rate in segment j
$R'_{i\lambda}$	inverse emission yield of element i at spectral line λ
$\mathfrak{R}'_{i\lambda}$	emission yield of element i at spectral line λ
$s'_{i\lambda}$	constant describing degree of non-linearity

A.2 Calculation of calibration constants using relative sputtering rates

Calibration is conducted using one of the following equations:

$$c_{iM} \times (q_M / q_{\mathrm{ref}}) = R_{i\lambda} \times I_{i\lambda} - B_\lambda \qquad \text{(A.1)}$$

or

$$c_{iM} = R_{i\lambda} \times I_{i\lambda} (q_{\mathrm{ref}} / q_M) - B_{\lambda\mathrm{rel}} \qquad \text{(A.2)}$$

where

c_{iM}	is the mass fraction of element i in sample M;
q_M/q_{ref}	is the sputtering rate of sample M relative to that of a reference sample;
q_M	is the sputtering rate expressed as the mass loss rate per unit area of sample M;
q_{ref}	is the sputtering rate expressed as the mass loss rate per unit area of a reference sample;
$R_{i\lambda}$	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 some more complex function, given in mass fraction units, provided by the manufacturer;

$B_{\lambda\text{rel}}$ is a different but related spectral background term at wavelength λ which is given, in Equation (A.2), in mass fraction units, is often referred to as the "background equivalent concentration" and may be treated as a constant or as some more complex function provided by the manufacturer (see also Note 2);

q_ref/q_M is equal to $1/(q_M/q_\text{ref})$ and is called the sputtering rate correction factor.

NOTE 1 The inverse emission yield is related to the emission yield $\Re_{i\lambda}$ by

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

where the emission yield is defined as

$$\Re_{i\lambda} \equiv (I_{i\lambda} - b_\lambda)/(c_{iM} \times q_M) \tag{A.4}$$

b_λ being the spectral background intensity at wavelength λ.

NOTE 2 The two spectral background terms are related by

$$B_{\lambda\text{rel}} = (q_\text{ref}/q_M) \times B_\lambda \tag{A.5}$$

These equations 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, second-order Equations (A.1) and (A.2) become, respectively

$$c_{iM} \times (q_M/q_\text{ref}) = R_{i\lambda} \times I_{i\lambda} + s_{i\lambda} \times I_{i\lambda}{}^2 - B_\lambda \tag{A.6}$$

and

$$c_{iM} = R_{i\lambda} \times I_{i\lambda} \times (q_\text{ref}/q_M) + s_{i\lambda} \times I_{i\lambda}{}^2 \times (q_\text{ref}/q_M) - B_{\lambda\text{rel}} \tag{A.7}$$

where $s_{i\lambda}$ is a constant 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 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 samples, the relative sputtering rates and the sputtering rate correction factors are both close to unity, and insensitive to plasma conditions.

NOTE 3 The spectral background terms in Equations (A.1) and (A.2) are not true constants, but are more or less matrix-dependent as was pointed out in 4.2.3.1. In practical work, it is always advisable to select the lowest measured intensity as the fixed background for each spectral line.

NOTE 4 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.3 Calculation of calibration constants using absolute sputtering rates

Calibration is conducted with one of the following equations:

$$c_{iM} \times q'_M = R'_{i\lambda} \times I_{i\lambda} - B'_\lambda \qquad \text{(A.8)}$$

or

$$c_{iM} = R'_{i\lambda} \times I_{i\lambda} / q'_M - B'_{\lambda\text{rel}} \qquad \text{(A.9)}$$

where

c_{iM} is the mass fraction of element i in sample M;

q'_M is the sputtering rate expressed as the mass loss rate of sample M;

$R'_{i\lambda}$ 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 some more complex function, given in mass fraction units multiplied by sputtering rate, provided by the manufacturer;

$B'_{\lambda\text{rel}}$ is a different but related spectral background term at wavelength λ which is given, in Equation (A.9), in mass fraction units, is often referred to as the “background equivalent concentration” and may be treated as a constant or as some more complex function provided by the manufacturer (see also Note 2).

NOTE 1 The inverse emission yield is related to the emission yield $\Re'_{i\lambda}$ by

$$R'_{i\lambda} = 1 / \Re'_{i\lambda} \qquad \text{(A.10)}$$

where the emission yield is defined as

$$\Re'_{i\lambda} \equiv \left(I_{i\lambda} - b_\lambda\right) / \left(c_{iM} \times q'_M\right) \qquad \text{(A.11)}$$

b_λ being the background intensity.

NOTE 2 The two spectral background terms are related by

$$B'_{\lambda\text{rel}} = B'_\lambda / q'_M \qquad \text{(A.12)}$$

These equations 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, second-order Equations (A.8) and (A.9) become, respectively

$$c_{iM} \times q'_M = R'_{i\lambda} \times I_{i\lambda} + s'_{i\lambda} \times I_{i\lambda}{}^2 - B'_{i\lambda} \qquad \text{(A.13)}$$

and

$$c_{iM} = R'_{i\lambda} \times I_{i\lambda} / q'_M + s'_{i\lambda} \times I_{i\lambda}{}^2 / q'_M - B'_{i\lambda\text{rel}} \qquad \text{(A.14)}$$

where $s'_{i\lambda}$ 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.

NOTE 3 The spectral background terms in Equations (A.8) and (A.9) are not true constants, but are more or less matrix-dependent as was pointed out in 4.2.3.1. In practical work, it is always advisable to select the lowest measured intensity as the fixed background for each spectral line.

NOTE 4 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 mass fractions and sputtered mass using relative sputtering rates

A.4.1 General

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

A.4.2 Calculation based on relative elemental sputtering rate

If a calibration function based on Equation (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 $[c_{iM} \times (q_M/q_{\text{ref}})]_j$ for each element i. 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 $(q_M/q_{\text{ref}})_j$ of segment j of the depth profile of sample M using the equation

$$(q_M / q_{\text{ref}})_j = \sum_i \left[c_{iM} \times (q_M / q_{\text{ref}}) \right]_j / 100 \tag{A.15}$$

The mass fraction c_{iMj} of element i in segment j is given by the equation

$$c_{iMj} = \left[c_{iM} \times (q_M / q_{\text{ref}}) \right]_j \Big/ (q_M / q_{\text{ref}})_j \tag{A.16}$$

where c_{iMj} is given in %.

The total sputtered mass per unit area, $M_{j\text{tot}}$, in segment j and in the corresponding time increment Δt_j is given by the equation

$$M_{j\text{tot}} = q_{\text{ref}} \times (q_M / q_{\text{ref}})_j \times \Delta t_j \tag{A.17}$$

A.4.3 Calculation based on the mass fractions of the elements

If a calibration function based on Equation (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 c_{iMj} of element i in segment j of sample M, expressed as mass %, is given by the equation

$$c_{iMj} = \frac{(k_{i\lambda} \times I_{i\lambda} - B_{\lambda\text{rel}})_j}{\sum_i (k_{i\lambda} \times I_{i\lambda} - B_{\lambda\text{rel}})_j} \times 100 \tag{A.18}$$

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

NOTE Equation (A.18) incorporates a sum normalization of all mass fractions to 100 %.

If non-linear calibration curves are used, replace the linear functions shown in Equation (A.18) by the corresponding non-linear functions.

For each segment j of the depth profile, calculate the sputtering rate per unit area q_{Mj} using the equation

$$q_{Mj} = q_{\text{ref}} \times \sum_i (k_{i\lambda} \times I_{i\lambda} - B_{\lambda\text{rel}})/100 \tag{A.19}$$

For each segment j and corresponding time increment Δt_j of the depth profile, the sputtered mass per unit area m_{iMj} of element i is given by the equation

$$m_{iMj} = q_{Mj} \times c_{iMj} \times \Delta t_j /100 \tag{A.20}$$

The total sputtered mass per unit area, $M_{j\text{tot}}$, in segment j is given by the equation

$$M_{j\text{tot}} = \sum_i m_{iMj} \tag{A.21}$$

A.5 Calculation of mass fractions and sputtered mass using absolute sputtering rates

A.5.1 General

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

A.5.2 Calculation based on elemental sputtering rate

If a calibration function based on Equation (A.8) 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 $(c_{iM} \times q'_M)_j$ 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'_{Mj} of segment j of the depth profile of sample M using the equation

$$q'_{Mj} = \sum_i (c_{iM} \times q'_M)_j /100 \tag{A.22}$$

The mass fraction c_{iMj} of element i in segment j of sample M is given by the equation

$$c_{iMj} = (c_{iM} \times q'_M)_j / q'_{Mj} \tag{A.23}$$

where c_{iMj} is given in %.

The total sputtered mass per unit area, $M_{j\text{tot}}$, in segment j and in the corresponding time increment Δt_j is given by the equation

$$\mathrm{M}_{j\text{tot}} = q'_{Mj} \times \Delta t_j / A_M \tag{A.24}$$

where A_M is the area of the crater on sample M.

A.5.3 Calculation based on the mass fractions of the elements

If a calibration function based on Equation (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, the mass fraction c_{iMj} of element i in segment j of sample M, expressed as mass %, is given by the equation

$$c_{iMj} = \frac{(k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda\text{rel}})_j}{\sum_i (k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda\text{rel}})_j} \times 100 \tag{A.25}$$

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

NOTE Equation (A.25) incorporates a sum normalization of all mass fractions to 100 %.

If non-linear calibration curves are used, replace the linear functions shown in Equation (A.25) by the corresponding non-linear functions.

For each segment j of the depth profile, calculate the sputtering rate q'_{Mj} using the equation

$$q'_{Mj} = \sum_i (k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda\text{rel}})/100 \tag{A.26}$$

For each segment j and corresponding time increment Δt_j of the depth profile, the sputtered mass M_{iMj} of element i is given by the equation

$$M_{iMj} = q'_{Mj} \times c_{iMj} \times \Delta t_j /100 \tag{A.27}$$

The total sputtered mass per unit area, $M_{j\text{tot}}$, in segment j is given by the equation

$$M_{j\text{tot}} = \sum_i M_{iMj} / A_M \tag{A.28}$$

A.6 Calculation of sputtered depth

A.6.1 General

The analytical method described in this International Standard 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, this 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 method.

A.6.2 Calculation based on constant atomic volume

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

$$\rho_j = 100 / \sum_i \frac{c_{iMj}}{\rho_i} \tag{A.29}$$

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 the equation

$$z_j = \frac{M_{j\text{tot}}}{\rho_j} \tag{A.30}$$

The total depth is determined by summing z_j over j using Equation (A.30). Though not strictly necessary, it is interesting to calculate the sputtering rate per unit area in segment j by dividing $M_{j\text{tot}}$ by Δt_j.

A.6.3 Calculation based on averaged density

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

$$a_{ij} = \frac{(c_{iMj} / w_i)}{\sum_i (c_{iMj} / w_i)} \tag{A.31}$$

where w_i is the atomic mass of element i.

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

$$\rho_j = \sum_i a_{ij} \times \rho_i \tag{A.32}$$

For each segment j of the depth profile, calculate the thickness z_j using Equation (A.30). The total depth is determined by summing z_j over j.

Annex B
(informative)

Suggested spectral lines for determination of given elements

Element	Wavelength nm	Estimated useful mass fraction range %	Comments
Zn	330,26	0,001 to 100	
Zn	334,50	0,001 to 100	
Zn	481,053	0,001 to 100	
Al	172,50	0,1 to 100	
Al	396,15	0,001 to 100[a]	Self-absorption
Ni	231,603	0,01 to 100	
Ni	341,78	0,001 to 100[a]	Weak self-absorption
Ni	349,30	0,005 to 100[a]	Weak self-absorption
Pb	202,20	0,001 to 10	
Pb	405,87	0,005 to 100	
Sb	206,83	0,005 to 2	
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

[a] Use a non-linear calibration curve.

Annex C
(informative)

Determination of coating mass per unit area

C.1 General

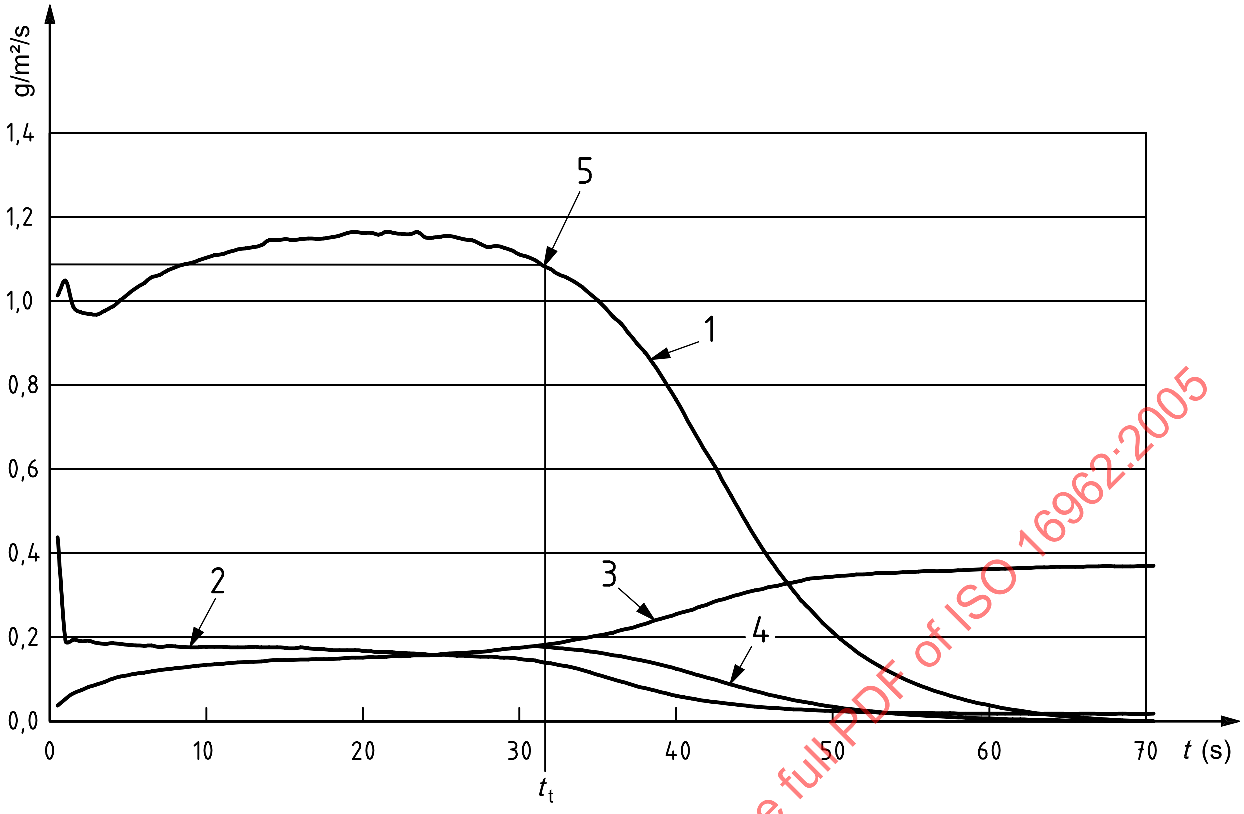
Coating mass per unit area can be calculated from the quantitative depth profile expressed in ordinate units of g/m^2/s and abscissa units of seconds. All commercial GD-OES spectrometer systems have provisions in the software for calculation of the coating mass per unit area for each individual element. This can be accomplished by summing the masses of each depth segment, obtained by Equation (A.16), (A.27) or (A.28), depending on the calculation method used. In instruments where it is available, the coating mass per unit area can also be calculated from the quantitative depth profile expressed in ordinate units of g/m^2/s and abscissa units of seconds. 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. 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 example in Figure C.1. In this example, Fe is the element of interest. Time t_t (when Fe in the base metal begins to appear) is assumed to be the time at which the ordinate value for the major element in the coating, Zn, falls to 95 % of its maximum or plateau-edge value. After time t_t, the Fe in the coating is assumed to decrease and reach zero in relation to the Zn profile. Therefore, the integral of Fe within the transition zone is equal to the integral of Zn between t_t and the time when the Zn profile falls below the detection limit for Zn, multiplied by the ratio of the Fe to Zn ordinate values at t_t. The total Fe coating mass per unit area is then the sum of the Fe coating mass per unit area within the transition zone and the integral of the Fe profile for all times prior to t_t.

NOTE An alternative definition of t_t 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 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 time at which the ordinate value falls to that characteristic of the substrate.



Key

1 Zn
2 Al in coating
3 Fe
4 Fe in coating
5 95 % of maximum Zn

Figure C.1 — Quantitative depth profile, expressed as g/m²/s vs seconds, illustrating method 1 for galvanneal

C.3 Method 2

C.3.1 Procedure for calculation of depth profile in units of g/m²/s versus seconds

Like the preceding method, method 2 is best explained by means of a galvanneal example (see Figure C.2). Time t_s is defined as the time at which the ordinate value for the major coating element Zn becoms equal to that of Fe. Time t_L is taken to be the time corresponding to the integration depth defined in 7.2 c). The Fe coating mass per unit area is then calculated, in g/m², as follows:

$$\text{Fe coating mass per unit area} = \text{Fe}_{0 \text{ to } t_s} - \alpha \times \text{Zn}_{t_s \text{ to } t_L}$$

where

$\text{Fe}_{0 \text{ to } t_s}$ is the value obtained by integrating the Fe profile from time zero to time t_s;

$\text{Zn}_{t_s \text{ to } t_L}$ is the value obtained by integrating the Zn profile from time t_s to time t_L;

α is an adjustment factor.