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## Surface chemical analysis — Analysis of metal oxide films by glow-discharge optical-emission spectrometry

*Analyse chimique des surfaces — Analyse de films d'oxyde de métal  
par spectrométrie d'émission optique à décharge lumineuse*





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## 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.

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](http://www.iso.org/directives)).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

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/TS 25138:2010), which has been technically revised. The main changes compared to the previous edition are as follows:

- the element Zr has been added to the Scope;
- the description of the apparatus has been modified to include spectrometers with solid-state array detectors of the types CCD and CID;
- [Clause 6](#) has been modified for more clarity, and to include the spectrometer types;
- [Clause 8](#) has been modified for more clarity, particularly in the recommendations for calibration samples.

A list of all parts in the ISO TS 25138 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).



# Surface chemical analysis — Analysis of metal oxide films by glow-discharge optical-emission spectrometry

## 1 Scope

This document describes a glow-discharge optical-emission spectrometric method for the determination of the thickness, mass per unit area and chemical composition of metal oxide films.

This method is applicable to oxide films 1 nm to 10 000 nm thick on metals. The metallic elements of the oxide can include one or more from Fe, Cr, Ni, Cu, Ti, Si, Mo, Zn, Mg, Mn, Zr and Al. Other elements that can be determined by the method are O, C, N, H, P and S.

## 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 14707, *Surface chemical analysis — Glow discharge optical emission spectrometry (GD-OES) — Introduction to use*

ISO 16962:2017, *Surface chemical analysis — Analysis of zinc- and/or aluminium-based metallic coatings by glow-discharge optical-emission spectrometry*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <http://www.electropedia.org/>

### 3.1 verification

confirmation, through the provision of objective evidence, that specified requirements have been fulfilled

[SOURCE: ISO 9000:2015, 3.8.12]

### 3.2 validation

confirmation, through the provision of objective evidence, that the particular requirements for a specific intended use or application have been fulfilled

[SOURCE: ISO 9000:2015, 3.8.13]

## 4 Principle

The analytical method described here involves the following processes.

- a) Cathodic sputtering of the surface metal oxide 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 spectral-emission lines of the analyte atoms as a function of sputtering time (qualitative depth profiling).
- 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.
- e) 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).

## 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<sup>[1]</sup> 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 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 principle of determination is based on continuous sputtering of the surface metal oxide, 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.

#### 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 samples. For applications where several 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 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 samples and higher power during analysis; therefore the sample 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 metal oxide. 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 samples due to e.g. surface layers of poor heat conductivity and/or very thin samples. In such cases, the smaller 2 mm anode 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 samples; hence this is the only type that can be used for e.g. polymer coatings and insulating oxide layers. 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 instrument. 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** It should be noted in this context that what is known as the emission yield<sup>[2][3]</sup> 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<sup>[8]</sup>. It is impossible in practice to maintain all three parameters constant for all test samples, 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<sup>[8]</sup>, 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 an optical system with photomultiplier detectors in fixed spectral positions, 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. For further information, see ISO 14707. For an optical system with CCD detectors, the corresponding control is to check that the wavelength calibration is correct, following the procedure given by the instrument manufacturer.

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 sample, to reduce the analysis time without overheating the sample;
- 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 the following subclauses.

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

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.

### 6.2.1.1 Setting the high voltage of the detectors

Select test samples with surface layers of all types to be determined. For all test samples, 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 and CID), adjust the integration time in the same way as the high voltage for PMT.

### 6.2.1.2 Adjusting the source 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 metal oxide 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 metal oxide 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 sample surface layers; sample cooling is beneficial in this regard.

### 6.2.1.3 Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a sample with a metal oxide typical of the test samples to be analysed to a depth of about 10 µm to 20 µm, but still inside the metal oxide. This is only possible for applications where surface metal oxide layers of such thickness are available. If no such sample is available, use a steel or brass sample. 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 sample, and adjust the pressure until a voltage of approximately 700 V is attained in the metal oxide.

Set the high voltage of the detectors as described in [6.2.1.1](#).

Adjust the discharge parameters as described in [6.2.1.2](#), adjusting first the current and, if necessary, the pressure.

Optimize the crater shape as described in [6.2.1.3](#) 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 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 the 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 of approximately 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 [6.2.1.1](#).

Adjust the source parameters as described in [6.2.1.2](#), adjusting first the voltage and if necessary the pressure.

Optimise the crater shape as described in [6.2.1.3](#), 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 RF voltage (the RF voltage is defined here as the RMS voltage at the coupling electrode without DC bias). In addition, the mode constant applied power and DC bias voltage is sometimes used, but less common. 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 voltage 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 commonly used for depth profiling of metal samples. Measure the penetration rate (i.e. depth per unit time) on an iron or steel sample, 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 [6.2.1.1](#).

Adjust the discharge parameters as described in [6.2.1.2](#), adjusting first the applied power and, if necessary, the pressure.

Optimize the crater shape as described in [6.2.1.3](#) 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 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 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, adjusting the power to give a penetration rate of about 2  $\mu\text{m}/\text{min}$  to 3  $\mu\text{m}/\text{min}$ .

Set the high voltage of the detectors as described in [6.2.1.1](#).

Adjust the discharge parameters as described in [6.2.1.2](#), adjusting first the applied power and, if necessary, the DC bias voltage.

Optimize the crater shape as described in [6.2.1.3](#) by adjusting the DC bias voltage.

Remeasure the penetration rate on the iron or steel sample and adjust the applied power, if necessary, to return to about 2  $\mu\text{m}/\text{min}$  to 3  $\mu\text{m}/\text{min}$ . 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.

**NOTE** This mode can only be used if conductive samples are measured, since the DC bias vanishes at non-conductive samples.

### 6.3.4 Constant effective power and 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 sample in place but without plasma (vacuum conditions). The RF voltage is defined here as the RMS voltage at the coupling electrode without DC bias.

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 W 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 [6.2.1.1](#).

Adjust the discharge parameters as described in [6.2.1.2](#), adjusting first the effective power and, if necessary, the RF voltage.

Optimize the crater shape as described in [6.2.1.3](#) 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 [6.4.2](#) and [6.4.3](#) 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 sample 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 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.

#### 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 metal oxides 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 metal oxide.

##### 6.4.3.2 SNR method

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

- 1) Select a bulk sample to be used as a blank. The composition of the sample should preferably be similar, in terms of the elemental composition of the matrix, to that of the metal oxides to be analysed. Further, the sample shall be known to contain less than 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 should preferably 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 unspattered area of the surface of the blank for each individual burn.
- 3) Compute the detection limit, expressed as a mass fraction, using the following formula:

$$DL = \frac{3 \times \sigma}{S} \quad (1)$$

where

DL is the detection limit;

$\sigma$  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 samples.

### 6.4.3.3 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 which has a matrix composition that is similar to that of the metal oxides 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 %.
- 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 should preferably 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 a freshly prepared 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 a freshly prepared area of the surface of the sample for each individual burn. Compute the average and the relative standard deviation of the ten replicate measurements.
- 4) Calculate the detection limit using the following formula:

$$DL = \frac{3 \times (w_A \times \sigma_{\text{Rel},B} / 100)}{(I - I_B) / I_B} \quad (2)$$

where

- DL is the detection limit;
- $w_A$  is the mass fraction of the analyte in the sample;
- $\sigma_{\text{Rel},B}$  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 samples.

## 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 samples taken 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. This is due to the fact that the 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 sample.

Rinse the surface of the sample 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 calibration formula as described in either [Clause A.2](#) or [Clause 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. The software of all commercially available spectrometers is designed to create several dedicated calibrations for different applications. A combination of a set of spectrometer system settings and a set of calibration equations valid at these settings is usually called an analytical method.

### 8.2 Calibration samples

#### 8.2.1 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 metal oxide materials in composition, but they shall have sputtering rates which are well determined and reproducible. In particular, samples of very low melting point (Zn, Sn, Pb) are not recommended, due to difficulties in obtaining reproducible and stable sputtering rates. 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 in regions of the spectrum where they do not have emission lines. 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 also be used.

**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 realisation 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® (SRM®) is a CRM issued by the National Institute of Standards and Technology, Gaithersburg, MD, USA.

#### 8.2.2 Low alloy iron or steel samples

Use steel samples with iron mass fractions that are greater than 98 %. The iron mass fraction for a given sample can be determined by subtracting the sum of the mass fractions for all other known elements from 100 %.



### 8.2.3 Stainless-steel samples

Use stainless-steel samples with nickel mass fractions in the range 10 % to 40 %, chromium mass fractions in the range 10 % to 40 %, molybdenum mass fractions in the range 0,5 % to 10 % and manganese mass fractions in the range 0,1 % to 3 %.

### 8.2.4 Nickel alloy samples

Use nickel-based alloy samples with nickel mass fractions that are greater than 50 %.

### 8.2.5 Copper alloy samples

Use copper alloy samples with copper mass fractions that are greater than 50 % and zinc mass fractions that are greater than 30 %.

### 8.2.6 Titanium alloy samples

Use titanium alloy samples with titanium mass fractions that are greater than 50 %.

### 8.2.7 Silicon samples

Use a nearly pure silicon sample, which may also be used to determine zero points for all analytes except silicon.

### 8.2.8 Aluminium alloy samples

Use aluminium alloy samples with aluminium mass fractions that are greater than 50 % and magnesium mass fractions in the range 0,1 % to 5 %.

### 8.2.9 High-oxygen samples

Use oxide or oxide-based samples with oxygen mass fractions that are greater than 10 %. Whenever possible, use samples with the same type of oxide as in the samples to be analysed.

### 8.2.10 High-carbon samples

Use cast-iron and/or tungsten carbide samples with carbon mass fractions in the range 2 % to 10 %. Silicon carbide also works well, and its carbon content is about 30 %.

### 8.2.11 High-nitrogen samples

Use nitride or nitride-based samples with nitrogen mass fractions that are greater than 2 %.

### 8.2.12 High-hydrogen samples

Use hydride samples with hydrogen mass fractions that are greater than 2 %.

### 8.2.13 High-purity copper samples

Use a high-purity copper sample for which the total of the mass fractions of all other analytes is less than 0,001 %. This sample can also be used to determine zero points for all analytes except copper. The reason to use these samples rather than pure iron is that copper has a spectrum dominated by just a few emission lines and very low background levels in most parts of the optical spectrum.

### 8.3 Validation samples

#### 8.3.1 General

Validation samples should be prepared in order to check the accuracy of the analytical results. The following sample types described in [8.3.2](#) to [8.3.6](#) are suggested, but other samples may be used where appropriate. Note that these samples can also be used as additional calibration samples.

#### 8.3.2 Hot-rolled low-alloy steel

Hot-rolled steel sheet with 3 µm to 10 µm thick oxide scale typically has a layer of FeO close to the steel interface, followed by Fe<sub>3</sub>O<sub>4</sub> making up the outer oxide layer. In some cases, an additional outermost layer consisting of Fe<sub>2</sub>O<sub>3</sub> can be present. Either a mixture of these phases and metallic iron or at least a subsection thereof is mixed throughout the oxide scale. The relative content of the phases can be determined by XRD analysis. The thickness can be determined by optical microscopy.

#### 8.3.3 Oxidized silicon wafers

Use oxidized silicon wafers with an oxide layer of the thickness specified by the manufacturer.

NOTE 1 These samples have a very high reflectivity, which can result in an increased Emission Yield due to back-reflected light from the sample surface. This results in an incorrect depth determination (too high). On the other hand, optical interference in the transparent oxide layer provide an alternative, more accurate method to determine the oxide thickness [\[16\]](#)[\[17\]](#).

#### 8.3.4 TiN-coated samples

Use metallic samples coated with TiN, the thickness of the coating being as specified by the manufacturer.

#### 8.3.5 Anodized Al<sub>2</sub>O<sub>3</sub> samples

Use metallic samples with anodized Al<sub>2</sub>O<sub>3</sub>, the thickness of the anodized layer being as specified by the manufacturer.

#### 8.3.6 TiO<sub>2</sub>-coated samples

Use metallic samples coated with TiO<sub>2</sub>, the thickness of the coating being as specified by the manufacturer.

### 8.4 Determination of the sputtering rate of calibration and validation 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:

- a) prepare the sample surface in accordance with the recommendations of the instrument manufacturer or using another appropriate procedure;
- b) adjust the glow-discharge parameters to those selected in [6.2](#) or [6.3](#);
- c) sputter the sample for a time estimated to result in a crater 20 µm to 40 µm deep, recording the total sputtering time;
- d) repeat c) several times if the sample surface area is sufficiently large, recording the total sputtering time for each crater;

- e) measure the average depth of each crater by means of an optical or mechanical profilometer device, performing at least 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 according to the method given by the profilometer manufacturer, when available with compensation for non-flat crater bottoms. See also NOTE 1.
  - 3) calculate the sputtered mass as the 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;
- 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 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 similar to NIST 1761 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 should have an accuracy in the depth calibration of better than 5 %.

If laboratory means 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 following the method of Archimedes. A pycnometer (a standard vessel for measuring and comparing the densities of liquids or solids) can also be used for accurate volume determination. Alternatively, the sample volume can be estimated from the sample dimensions or the density calculated from the sample composition as described in [Annex A](#) [see [Formula \(A.34\)](#)]. The accuracy of the measured or calculated density should be 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<sup>[14][15]</sup>.

NOTE 2 The sputtered mass can also be determined by weighing samples before and after sputtering. However, this requires the use of scales of extremely high accuracy, and the uncertainty in such measurements is generally inferior to that with crater depth measurements. It should also be noted that this procedure generally results in somewhat too low values for the sputtered mass, since re-deposited material outside the crater is also weighed. A correction for this effect should be applied if possible, but there is no standard procedure for such correction available.

NOTE 3 For calibration samples in the form of oxide and nitride films on a metal substrate, it is normally not possible to determine the density and sputtering rate directly as described above. In such cases, first identify the oxide type by available methods such as X-ray fluorescence spectroscopy (XPS) or X-ray diffraction (XRD), then use a tabulated value for the density found in the literature (see also [Annex C](#)). Determine the thickness of the oxide film by available methods such as light optical microscopy (LOM), scanning electron microscopy (SEM) or transmission electron microscopy (TEM). The sputtering rate is then determined from the time to sputter through the film, converted to a mass loss rate.

NOTE 4 The sputtering rates of certain RMs might be available from the instrument manufacturer or from the scientific literature.

## 8.5 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 ethanol 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](#) 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 sample at least two times and calculate the average values.

NOTE 1 For calibration samples in the form of oxide and nitride films on a metal substrate, the intensities cannot be measured with a fixed preburn time. Instead, the samples must be run in depth profile mode, and a time segment of the layer with nearly constant intensities selected. The average intensity in this segment is used for the calibration.

## 8.6 Calculation of calibration formulae

Perform the calibration computations in accordance with one of the calculation methods specified in either [Clause A.2](#) or [Clause A.3](#). For all commercially available GD-OES instruments, the software incorporates at least one of these calculation methods. They are all based on the assumption that the previously mentioned emission yield is a matrix-independent quantity at constant source parameters.<sup>[2]</sup> The fact that there exist more than one method based on this assumption is mainly historical, detailed calculation schemes have been developed independently by several researchers. For the purpose of this document, no preference is given to a particular calculation method.

Depending on the type of source, the mode of operation and the calibration samples chosen, the calibration formulae for some elements might show a large separation between samples of substantially different composition ("matrices"), e.g. between steels and aluminium alloys. 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 impedance. If some facility is provided by the instrument manufacturer to minimize this effect, it should be used. Otherwise the solution is to choose calibration samples which most resemble the samples to be analysed.

## 8.7 Validation of the calibration

### 8.7.1 General

Carry out the following procedure immediately after calibration in order to confirm that the calibration formulae 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 [8.8](#).

Two validation procedures are included in this clause. The first procedure (see [8.7.2](#)) makes use of bulk reference materials and the second (see [8.7.3](#)) employs metal oxide reference materials. Such metal oxide reference materials are often difficult to obtain. As a result, the validation procedure described in [8.7.3](#) is optional.

NOTE Validation of a method is defined in ISO/IEC 17025:2017, 7.2.2. Validation of the calibration is analogous to it (see the Note in [8.8](#)).

### 8.7.2 Checking analytical accuracy using bulk reference materials

- a) Select, in accordance with [8.2](#), an appropriate number of bulk reference materials to be used for validation of the calibration.
- b) Measure the emission intensities of these validation samples 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 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 formulae.
- 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, the disagreement shall be investigated. It might be necessary to repeat the calibration.

### 8.7.3 Checking analytical accuracy using metal oxide 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 metal oxide reference material for a sufficiently long time to ensure that the metal oxide is completely removed, and sputtering has continued well into the substrate.
- d) Follow this document for calculating the relationships intensity versus time (qualitative) and mass percent versus depth in micrometres (quantitative). Most GD-OES instruments are equipped with software that will automatically calculate these relationships at the end of each analysis.
- e) Compute, as described in [10.2](#), the average mass fractions of the metal and oxygen for each validation sample.
- f) Compute, as described in [10.2.1 a\)](#) or [10.2.2 a\)](#), the metal oxide depth.
- g) Confirm that the average mass fractions of the metal and oxygen, as well as the oxide depth measured in this way, agree with known values to within appropriate statistical bounds. If statistical disagreement is found, the disagreement shall be investigated. It might be necessary to repeat the calibration.
- h) 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 formulae are acceptable.
- i) If the validation is not successful, repeat the calibration.

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

## 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 formulae 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 test samples to be used for verification of the calibration. These samples 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 samples 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 sample, using a freshly prepared surface for each burn.
- c) Compute, using the calibration formulae, the average mass fractions of the analytes for each sample.
- 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 formula or correcting the emission intensities, as specified by the instrument manufacturer.

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

NOTE See also the Note in [8.7.1](#).

## 9 Analysis of test samples

### 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 sample 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 oxide layers of the samples. 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 sample has a very thin oxide 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 samples

Calculate quantified depth profiles, using the calibration formulae established in accordance with [Clause A.7](#), in accordance with one of the calculation procedures described in [Annex A](#).

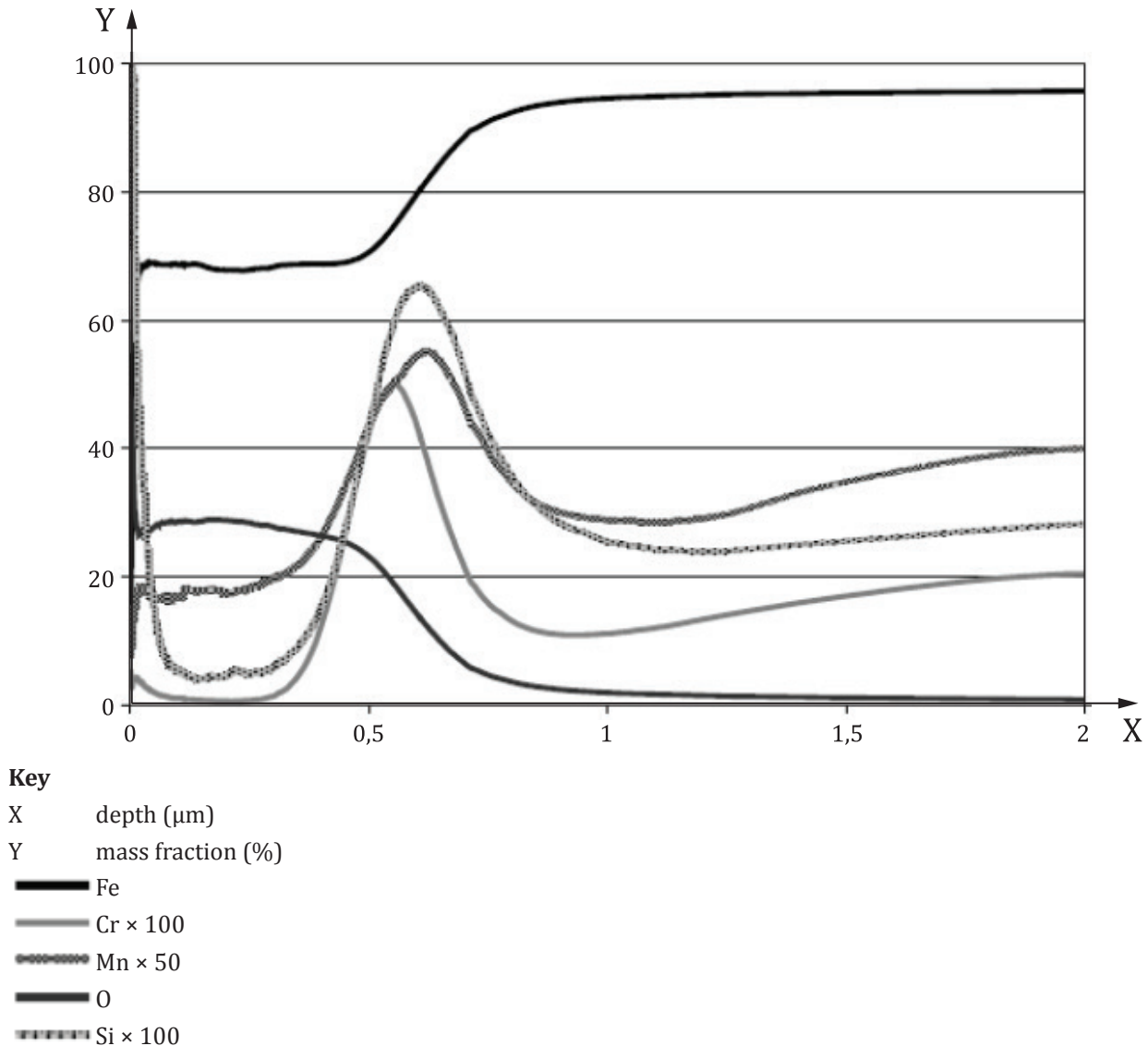
In order to determine the thickness of the oxide film accurately, it is often advisable to use special techniques to determine the density of the oxide, based on tabulated values of pure oxides. Two alternative techniques for doing this are described in [Clause A.8](#).



## 10 Expression of results

### 10.1 Expression of quantitative depth profile

An example of a quantitative depth profile is shown in [Figure 1](#).



**Figure 1 — Quantitative depth profile of an oxide on an annealed cold-rolled steel**

### 10.2 Determination of metal oxide mass per unit area

**10.2.1** In cases where the metal oxide layer consists entirely of elements which are also present in very low concentrations in the substrate material (e.g. titanium oxide on a steel substrate), the metal oxide mass is calculated by integration of the depth profile for each element, using the relevant algorithms given in [Clause A.6](#) or [Clause A.7](#). It is important to carry out the integration for elements present in the oxide only.

The following general recommendations are given for the determination of the integration depth.

- Define the metal oxide thickness as the distance from the surface to the depth at which the mass fraction of the major metallic element is reduced to 50 % of the “plateau” value in the metal oxide.

- b) Define the width of the interface as the difference between the two points in depth where the mass fractions of the major metallic element are 84 % and 16 % of the “plateau” value in the metal oxide. The “plateau” value will have to be estimated by the analyst in cases where the oxide is not quite homogeneous or is very thin.
- c) Take as the integration depth the sum of the metal oxide thickness and the interface width.

**10.2.2** In cases where the major metallic element of the oxide is the same as that of the substrate (e.g. iron oxide on a steel substrate), the metal oxide mass is calculated by integration of the depth profile for each element, using the relevant algorithms given in [Clause A.6](#) or [Clause A.7](#) and in ISO 16962:2017, Annex C, Clause C.2 (method 1). It is important to carry out the integration for elements present in the oxide only.

The following general recommendations are given for the determination of the integration depth:

- a) Define the metal oxide thickness as the distance from the surface to the depth at which the mass fraction of the major metallic element reaches a “plateau” value.
- b) Identify the two points where the mass fraction of the major metallic element is 1) the mass fraction in the metal oxide plus 16 % and 2) 84 % of the difference between the mass fraction in the metal oxide and that in the metallic substrate. Define the width of the interface as the difference in depth between these two points. This is analogous to the definition in [10.2.1](#) above.
- c) Take as the integration depth the sum of the metal oxide thickness and the interface width.

**10.2.3** Alternatively, by determination of the oxygen mass per unit area, the total oxide mass per unit area can usually be estimated from the composition of the oxide.

NOTE The composition and density of several common metal oxides are given in [Annex C](#).

### 10.3 Determination of the average mass fractions of the elements in the oxide

The average mass fraction of each element in the metal oxide is determined by dividing the integrated mass per unit area for the element (within the integration depth determined as described in [10.2](#)) by the total metal oxide mass per unit area. In cases where the major metallic element of the oxide is the same as that of the substrate (e.g. iron oxide on a steel substrate), this requires that the determination of the mass per unit area of the metallic element be carried out in accordance with ISO 16962:2017, Annex C, Clause C.2 (method 1).

## 11 Precision

An interlaboratory trial of this method was carried out by six laboratories, using nine samples, each laboratory making two quantitative depth profiles of each sample. The test samples used are listed in [Table D.1](#) in [Annex D](#). The metal oxide thickness was determined as described in [10.2.1](#) a) and the oxygen mass fraction was determined as described in [10.3](#). In addition, the oxide thickness was calculated from the oxygen mass (or the mass of the metal oxide component) and the assumed oxide composition, based on identification of the oxide type from the depth profile or other information about the sample.

When possible, FIB-SEM (focussed ion beam scanning electron microscope) images of cross sections of the oxide layers were also studied for comparison. The thickness was measured at several points and compared with the results of GD-OES. This comparison is shown in [Tables D.2](#) to [D.10](#). The comparison shows that, for most samples, the oxide thickness determined by GD-OES is correct within the statistical uncertainty, but it is not possible to conclude which of the two methods gives the more precise results.

Due to the limited number of results from the interlaboratory trial, it is not meaningful to subject the data to further statistical analysis than that shown in [Annex D](#). The precision of the method shall therefore be estimated for each application, based on available samples for verification.



## 12 Test report

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

- a) all information necessary for the identification of the sample;
- b) the laboratory and the date of the analysis;
- c) a reference to this document;
- d) the analytical results and the form in which they have been expressed;
- e) any unusual features noted during the determination;
- f) details of any operation not specified in this document, as well as of any optional operation, which may have influenced the results.

## Annex A (informative)

### 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 $j$
$A_D$	area of sputtering crater on sample D
$I_{i\lambda}$	emission intensity at wavelength $\lambda$ of element $i$
$I_{B\lambda}$	average background intensity at wavelength $\lambda$ ;
$m_{iDj}$	sputtered mass per unit area of element $i$ in segment $j$ of sample D
$m_{j\text{tot}}$	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
$s_{\text{cal}}$	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 sample D
$U_{\text{av}}$	average voltage recorded for the set of calibration samples used
$U_{\text{cal}}$	voltage used for the calibration of the method
$w_{iD}$	mass fraction of element $i$ in sample D
$w_{iDj}$	mass fraction of element $i$ in depth segment $j$ of sample D
$W_i$	atomic mass of element $i$
$z_j$	thickness of segment $j$
$\Delta_{tj}$	time increment corresponding to depth segment $j$
$\rho_i$	density of pure element $i$
$\rho_j$	density of segment $j$

**A.1.2 Symbols used in [Clauses A.2](#) and [A.6](#) concerned with relative sputtering rates**

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

**A.1.3 Symbols used in [Clauses A.3](#) and [A.7](#) concerned with absolute sputtering rates**

$B'_{\lambda}$	spectral background term at wavelength $\lambda$ , expressed as a mass fraction multiplied by the sample sputtering rate
$B'_{\lambda\text{rel}}$	related spectral background term at wavelength $\lambda$ , expressed as a mass fraction
$e'_{i\lambda}$	constant describing the degree of non-linearity for element $i$ at spectral line $\lambda$
$k'_{i\lambda}$	factor derived from the inverse emission yield divided by the sputtering rate
$q'_{\text{D}}$	sputtering rate of sample D
$q'_{\text{D}j}$	sputtering rate in segment $j$ of sample D
$R'_{i\lambda}$	inverse emission yield of element $i$ at spectral line $\lambda$
$\mathfrak{R}'_{i\lambda}$	emission yield of element $i$ at spectral line $\lambda$

**A.2 Calculation of calibration constants using relative sputtering rates**

Calibration is conducted using one of the following formulae:

$$w_{i\text{D}} \times (q_{\text{D}}/q_{\text{ref}}) = R_{i\lambda} \times I_{i\lambda} - B_{\lambda} \quad (\text{A.1})$$

or

$$w_{i\text{D}} = R_{i\lambda} \times I_{i\lambda} \times (q_{\text{ref}}/q_{\text{D}}) - B_{\lambda\text{rel}} \quad (\text{A.2})$$

where

- $w_{iD}$  is the mass fraction of element  $i$  in sample D;
- $q_D/q_{\text{ref}}$  is the sputtering rate of sample D relative to that of a reference sample;
- $q_D$  is the sputtering rate expressed as the mass loss rate per unit area of sample D;
- $q_{\text{ref}}$  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  $\lambda$  (see also Note 1);
- $I_{i\lambda}$  is the emission intensity of element  $i$  at spectral line  $\lambda$ ;
- $B_\lambda$  is a spectral background term at wavelength  $\lambda$ ;
- $B_{\lambda\text{rel}}$  is a different but related spectral background term at wavelength  $\lambda$  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);
- $q_{\text{ref}}/q_D$  is equal to  $1/(q_D/q_{\text{ref}})$  and is called the sputtering-rate correction factor.

NOTE 1 The inverse emission yield is related to the emission yield,  $\mathfrak{R}_{i\lambda}$ , by:

$$R_{i\lambda} = 1 / (q_{\text{ref}} \times \mathfrak{R}_{i\lambda}) \quad (\text{A.3})$$

where the emission yield is defined as:

$$\mathfrak{R}_{i\lambda} \equiv (I_{i\lambda} - I_{B\lambda}) / (w_{iD} \times q_D) \quad (\text{A.4})$$

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

NOTE 2 The two spectral background terms are related by:

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

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, [Formula \(A.1\)](#) and [\(A.2\)](#) can be expressed, with such second-order terms, as shown in [Formula \(A.6\)](#) and [\(A.7\)](#), respectively:

$$w_{iD} \times (q_D / q_{\text{ref}}) = R_{i\lambda} \times I_{i\lambda} + e_{i\lambda} \times I_{i\lambda}^2 - B_\lambda \quad (\text{A.6})$$

and

$$w_{iD} = R_{i\lambda} \times I_{i\lambda} \times (q_{\text{ref}} / q_D) + e_{i\lambda} \times I_{i\lambda}^2 \times (q_{\text{ref}} / q_D) - B_{\lambda\text{rel}} \quad (\text{A.7})$$

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  $q_{\text{ref}}$  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 the plasma conditions.

The spectral background terms in [Formula \(A.1\)](#) 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.3 Calculation of calibration constants using absolute sputtering rates

Calibration is conducted using one of the following formulae:

$$w_{iD} \times q'_D = R'_{i\lambda} \times I_{i\lambda} - B'_\lambda \quad (\text{A.8})$$

or

$$w_{iD} = R'_{i\lambda} \times I_{i\lambda} / q'_D - B'_{\lambda\text{rel}} \quad (\text{A.9})$$

where

- $w_{iD}$  is the mass fraction of element  $i$  in sample D;
- $q'_D$  is the sputtering rate, expressed as the mass loss rate, of sample D;
- $R'_{i\lambda}$  is the inverse emission yield of element  $i$  at spectral line  $\lambda$  (see also Note 1);
- $I_{i\lambda}$  is the emission intensity of element  $i$  at spectral line  $\lambda$ ;
- $B'_\lambda$  is a spectral background term at wavelength  $\lambda$  which may be treated as a constant or as a more complex function, expressed as a mass fraction multiplied by the sample sputtering rate, provided by the manufacturer;
- $B'_{\lambda\text{rel}}$  is a different but related spectral background term at wavelength  $\lambda$  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:

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

where the emission yield is defined as:

$$\mathfrak{R}'_{i\lambda} = (I_{i\lambda} - I_{B\lambda}) / (w_{iD} \times q'_D) \quad (\text{A.11})$$

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

NOTE 2 The two spectral background terms are related by:

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

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, [Formula \(A.8\)](#) and [\(A.9\)](#) can be expressed, with such second-order terms, as shown in [Formula \(A.13\)](#) and [\(A.14\)](#), respectively:

$$w_{iD} \times q'_D = R'_{i\lambda} \times I_{i\lambda} + e'_{i\lambda} \times I_{i\lambda}^2 - B'_{i\lambda} \quad (\text{A.13})$$

and

$$w_{iD} = R'_{i\lambda} \times I_{i\lambda} / q'_D + e'_{i\lambda} \times I_{i\lambda}^2 / q'_D - B'_{i\lambda\text{rel}} \quad (\text{A.14})$$

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 [Formula \(A.8\)](#) 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.4 Correction of elemental intensities and sputtered mass for variations in discharge parameters

### A.4.1 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.4.2 Correction of elemental intensities based on tabulated constants for discharge parameters

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

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

where

$a_\lambda$  is a factor characteristic of spectral line  $\lambda$ ;

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

$s_j$  is the current in segment  $j$ ;

$s_0$  is the reference current given by the instrument manufacturer.

Tabulated values of the exponential constant,  $a_\lambda$ , 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 [Formula \(A.8\)](#), [\(A.9\)](#), [\(A.13\)](#) and [\(A.14\)](#) instead of  $I_{i\lambda}$ .

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

### A.4.3 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 the formula:

$$R_{i\lambda}'' = 1 + r_{i\lambda}^U (U_D - U_{av}) \quad (\text{A.16})$$

where

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

$U_D$  is the voltage recorded for calibration sample D;

$U_{av}$  is the average voltage recorded for the set of calibration samples 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 be added to those described below.

The requirements for implementing the voltage correction are that

- the source be operated at constant pressure;
- either the DC bias voltage or the applied voltage be measured during calibration and analysis;
- a sufficient number of calibration samples giving substantial variation in the operating voltage be used for calibration.

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

### A.4.4 Correction of sputtering rate for variations in discharge parameters

If corrections for intensity variations are carried out in accordance with [A.4.2](#), 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,  $q'_{\text{ref}}$ , of the reference sample in accordance with:

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

where

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

$U_{\text{cal}}$  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 sample,  $q'_{\text{ref}}$ , is then inserted into [Formula \(A.20\)](#) and [\(A.22\)](#) below instead of  $q_{\text{ref}}$ .

## A.5 Correction of emission yields due to the influence of hydrogen

### A.5.1 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.5.2 Correction of elemental intensities based on reference hydrogen intensity and tabulated constants

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

$$I''_{i\lambda} = I'_{i\lambda} \exp\left(b_{\lambda} \frac{I_H}{I_{H\text{ref}}}\right) \quad (\text{A.18})$$

where

$b_{\lambda}$  is a constant characteristic of spectral line  $\lambda$ ;

$I_H$  is the observed hydrogen emission intensity;

$I_{H\text{ref}}$  is the hydrogen emission intensity from a reference material, e.g. a  $\text{TiH}_2$  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 [Clauses A.6](#) to [A.7](#).

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

### A.5.3 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 the following formula:

$$R''_{i\lambda} = r_{i\lambda}^H (1 + I_{\text{HD}}) \quad (\text{A.19})$$

where

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

$I_{\text{HD}}$  is the hydrogen intensity recorded for calibration sample 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 samples shall include at least one sample with substantial hydrogen content;



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

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

## A.6 Calculation of mass fractions and sputtered mass using relative sputtering rates

### A.6.1 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.6.2 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  $[w_{iD} \times (q_D/q_{ref})]_j$  for each element,  $i$ , of sample 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,  $(q_D/q_{ref})_j$ , of segment  $j$  of the depth profile of sample D using the formula:

$$(q_D/q_{ref})_j = \sum_i [w_{iD} \times (q_D/q_{ref})]_j / 100 \quad (\text{A.20})$$

The mass fraction,  $w_{iDj}$ , of element  $i$  in segment  $j$  of sample D is given by the following formula:

$$w_{iDj} = [w_{iD} \times (q_D/q_{ref})]_j / (q_D/q_{ref})_j \quad (\text{A.21})$$

where  $w_{iDj}$  is expressed in percent.

The total sputtered mass per unit area,  $m_{j\text{tot}}$ , in segment  $j$  and in the corresponding time increment,  $\Delta t_j$ , is given by the following formula:

$$m_{j\text{tot}} = q_{\text{ref}} \times (q_D/q_{\text{ref}})_j \times \Delta t_j \quad (\text{A.22})$$

### A.6.3 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,  $w_{iDj}$ , of element  $i$  in segment  $j$  of sample D, expressed in percent, is given by the following formula:

$$w_{iDj} = \frac{(k_{i\lambda} \times I_{i\lambda} - B_{\lambda\text{rel}})_j}{\sum_i (k_{i\lambda} \times I_{i\lambda} - B_{\lambda\text{rel}})_j} \times 100 \quad (\text{A.23})$$

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

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 sample D, calculate the sputtering rate per unit area,  $q_{Dj}$ , using the following formula:

$$q_{Dj} = q_{\text{ref}} \times \sum_i (k_{i\lambda} \times I_{i\lambda} - B_{\lambda\text{rel}}) / 100 \quad (\text{A.24})$$

For each segment,  $j$ , and corresponding time increment,  $\Delta t_j$ , of the depth profile of sample D, the sputtered mass per unit area,  $m_{iDj}$ , of element  $i$  is given by the following formula:

$$m_{iDj} = q_{Dj} \times w_{iDj} \times \Delta t_j / 100 \quad (\text{A.25})$$

The total sputtered mass per unit area,  $m_{j\text{tot}}$ , in segment  $j$  is given by the following formula:

$$m_{j\text{tot}} = \sum_i m_{iDj} \quad (\text{A.26})$$

## A.7 Calculation of mass fractions and sputtered mass using absolute 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 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 sample D, calculate from the calibration function the quantity  $(w_{iD} \times q'_D)_j$  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,  $q'_{Dj}$ , of segment  $j$  of the depth profile of sample D using the following formula:

$$q'_{Dj} = \sum_i (w_{iD} \times q'_D)_j / 100 \quad (\text{A.27})$$

The mass fraction,  $w_{iDj}$ , of element  $i$  in segment  $j$  of sample D is given by the following formula:

$$w_{iDj} = (w_{iD} \times q'_D)_j / q'_{Dj} \quad (\text{A.28})$$

where  $w_{iDj}$  is expressed in per cent.

The total sputtered mass per unit area,  $m_{j\text{tot}}$ , in segment  $j$  and in the corresponding time increment,  $\Delta t_j$ , is given by the following formula:

$$m_{j\text{tot}} = q'_{Dj} \times \Delta t_j / A_D \quad (\text{A.29})$$

where  $A_D$  is the area of the crater on sample D.

### A.7.3 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,  $w_{iDj}$ , of element  $i$  in segment  $j$  of sample D, expressed as a mass fraction in per cent, using the following formula:

$$w_{iDj} = \frac{(k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda})_j}{\sum_i (k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda})_j} \times 100 \quad (\text{A.30})$$

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

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,  $q'_{Dj}$ , using the following formula:

$$q'_{Dj} = \sum_i (k'_{i\lambda} \times I_{i\lambda} - B'_{\lambda}) / 100 \quad (\text{A.31})$$

For each segment,  $j$ , and corresponding time increment,  $\Delta t_j$ , of the depth profile, the sputtered mass,  $m_{iDj}$ , of element  $i$  is given by the following formula:

$$m_{iDj} = q'_{Dj} \times w_{iDj} \times \Delta t_j / 100 \quad (\text{A.32})$$

The total sputtered mass per unit area,  $m_j$ , in segment  $j$  is given by the following formula:

$$m_j = \sum_i m_{iDj} / A_D \quad (\text{A.33})$$

## A.8 Calculation of sputtered depth

### A.8.1 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.8.2 Calculation based on constant atomic volume

For each segment,  $j$ , of the depth profile of sample D, calculate the density,  $\rho_j$ , using the following formula:

$$\rho_j = 100 / \sum_i \frac{w_{iDj}}{\rho_i} \quad (\text{A.34})$$

where  $\rho_i$  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 following formula:

$$z_j = \frac{m_{j\text{tot}}}{\rho_j \times A_D} \quad (\text{A.35})$$

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  $m_{j\text{tot}}$  by  $\Delta t_j$ .

NOTE An alternative to utilizing a known value of the oxide density is to calculate the quantity  $\rho_0$  as follows:

$$\rho_0 = w_{\text{OD}j} / \left( 100 / \rho_j - w_{iDj} / \rho_i \right) \quad (\text{A.36})$$

where

$w_{\text{OD}j}$  is the mass fraction of oxygen in the oxide in segment  $j$  of sample D;

$\rho_j$  is the density of the oxide in segment  $j$ ;

$w_{iDj}$  is the mass fraction of pure metal element  $i$  in the oxide in segment  $j$  of sample D;

$\rho_i$  is the density of pure metal element  $i$  in the oxide.

Values of  $\rho_0$  for several oxides are given in [Annex C](#). If the spectrometer software has provisions for manual input of density, insert the relevant value of  $\rho_0$  obtained from [Formula \(A.36\)](#) in the time interval the oxide is sputtered.

### A.8.3 Calculation based on averaged density

For each segment,  $j$ , of the depth profile of sample D, calculate the atomic fraction,  $A_{ij}$ , of each element,  $i$ , using the following formula:

$$A_{ij} = \frac{(w_{iDj} / W_i)}{\sum_i (w_{iDj} / W_i)} \quad (\text{A.37})$$

where  $W_i$  is the atomic mass of element  $i$ .

For each segment,  $j$ , of the depth profile, calculate the estimated density,  $\rho_j$ , using the following formula:

$$\rho_j = \sum_i A_{ij} \times \rho_i \quad (\text{A.38})$$

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)

### Suggested spectral lines for determination of given elements

Element	Wavelength nm	Estimated useful mass fraction range %	Comments
O	130,22	0,1 to 100	This line has been found to be matrix-dependent, e.g. Iron and Aluminium oxides cannot have a common calibration.
O	777,19	1 to 100	
H	121,57	0,1 to 100	
H	656,28	1 to 100	
N	149,26	0,01 to 100	
N	174,52	0,05 to 100	
C	156,14	0,005 to 100	
C	165,70	0,005 to 100	
P	178,28	0,005 to 10	
P	185,90	Not determined	
S	180,73	0,005 to 10	
S	189,05	Not determined	
Al	172,50	0,1 to 100	
Al	396,15	0,001 to 100 <sup>a</sup>	Self-absorption
Ni	225,386	0,01 to 100	
Ni	231,603	0,01 to 100	
Ni	341,78	0,001 to 100 <sup>a</sup>	Weak self-absorption
Ni	349,30	0,005 to 100 <sup>a</sup>	Weak self-absorption
Cr	267,72	0,01 to 100	
Cr	425,43	0,001 to 20	Strong self-absorption
Ti	339,279	0,005 to 100	
Ti	365,35	0,005 to 100	
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 <sup>a</sup>	Weak self-absorption
Fe	379,50	0,01 to 100	
Zn	213,856	0,001 to 100	Self-absorption
Zn	330,26	0,001 to 100	

<sup>a</sup> Use a non-linear calibration curve.

Element	Wavelength nm	Estimated useful mass fraction range %	Comments
Zn	334,50	0,001 to 100	
Zn	481,053	0,001 to 100	
Cu	296,12	0,01 to 100	
Cu	327,40	0,001 to 5 <sup>a</sup>	Strong self-absorption
Mg	277,67	0,001 to 5	Strong self-absorption
Mg	383,83	0,005 to 10	
Mn	279,48	0,005 to 10	
Mn	403,076	0,005 to 100	
Mo	379,83	Not determined	
Mo	386,41	0,001 to 10	
<sup>a</sup> Use a non-linear calibration curve.			

## Annex C

### (informative)

#### Examples of oxide density and the corresponding quantity $\rho_0$

Oxide	Density g/cm <sup>3</sup>	$\rho_0$ g/cm <sup>3</sup>
Al <sub>2</sub> O <sub>3</sub>	3,987	8,614
Cr <sub>2</sub> O <sub>3</sub>	5,225	3,282
Fe <sub>2</sub> O <sub>3</sub>	5,275	2,981
Fe <sub>3</sub> O <sub>4</sub>	5,200	2,751
NiO	6,809	3,648
SiO <sub>2</sub>	2,201	2,101
SiO <sub>2</sub>	4,287	16,268
TiO <sub>2</sub>	4,245	3,913
Ti <sub>2</sub> O <sub>3</sub>	4,574	4,730



## Annex D (informative)

### Report on interlaboratory testing of metal oxide films

#### D.1 General

The data in [Tables D.1](#) and [D.2](#) were derived from the results of international analytical testing carried out in 2007 and 2008 on nine metal oxide samples in six laboratories.

The test samples used are given in [Table D.1](#) and the results obtained for the metal oxide thickness and the oxygen mass fraction are given in [Tables D.2](#) to [D.10](#).

#### D.2 Description of samples included in the trial

**Table D.1 — Sample types, approximate thickness of the oxides and additional information**

Sample designation	Type of thin film	Approximate thickness	Additional information
1. Oxidized low-alloy steel	Mainly Fe oxide, with inter-face segregation of several alloying elements	0,5 µm	The two sides are equivalent DC/RF
2. 1650 SM (heat-treated high-alloy steel)	Complex mixed oxide with segregation of several elements, Ti-rich	30 nm	Analyse on unmarked side DC/RF
3. 13 RM 19 (high-alloy steel)	Passivation layer, rich in Fe, Cr, Ni, Mn	2 nm	The two sides are equivalent DC/RF
4. Al oxide on low-alloy steel	Al oxide with slight segregation of other elements	250 nm to 350 nm	Analyse on unmarked side RF/(DC)
5. Ti oxide on 18/8 steel (blue)	Ti oxide with slight segregation of other elements	40 nm to 65 nm	Analyse blue side RF/(DC)
6. Ti oxide on 18/8 steel (green)	Ti oxide with slight segregation of other elements	100 nm	Analyse green side RF
7. FeCrAl	Passivation layer, probably rich in the major elements	1 nm to 5 nm	The two sides are equivalent. The sample is very thin and requires mounting on a suitable backing plate. DC/RF
8. Oxidized Si	SiO <sub>2</sub>	230 nm	The two sides are equivalent. The supply of these samples is limited, therefore circulation of them to several labs will be necessary. RF
9. Anodized alumina with Cr marker layer	Oxide with Cr “spike” embedded	0,35 µm of oxide, a few nm of Cr spike at approx. 0,05 µm	To be analysed on the marked side RF

### D.3 Determination of oxide film thickness

#### D.3.1 Results for sample 1 (low-alloy oxidized steel)

Six laboratories participated and three laboratories submitted DC/RF data. Nine results are reported. In [Table D.2](#), the results being given for oxygen mass, oxygen mass fraction and oxide thickness. The oxide thickness is given as evaluated directly from the graphs and as calculated from the oxygen mass on the assumption that the oxide is of the type  $\text{Fe}_3\text{O}_4$ .

**Table D.2 — Results for sample 1**

	Oxygen mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxide thickness from oxygen mass nm	Oxygen mass fraction %
No. of results	9	9	9	9
Average	780	479	556	27
Standard deviation	162	88	116	5
Relative standard deviation (%)	21	18	21	18

An FIB-SEM image of a cross section of the oxide layer was studied. The thickness was measured at several points ranging from 345 nm to 610 nm. The results show that the oxide thickness determined by GD-OES is correct within the statistical uncertainty, but it is not possible to say which of the two methods used in [Table D.2](#) is the more precise.

#### D.3.2 Results for sample 2 (annealed high-alloy 1650 SM steel)

Six laboratories participated, and three laboratories submitted DC/RF data. Nine results were reported. In [Table D.3](#), the results are given for oxygen and titanium mass, oxygen mass fraction and oxide thickness. The oxide thickness is given as evaluated directly from the graphs and as calculated from the oxygen mass on the assumption that the oxide is of the type  $\text{Fe}_3\text{O}_4$ , an assumption that obviously can only be partially true in this case.

**Table D.3 — Results for sample 2**

	Oxygen mass mg/m <sup>2</sup>	Titanium mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxide thickness from oxygen mass nm	Oxygen mass fraction %
No. of results	9	9	9	9	9
Average	55	26	27	39	37
Standard deviation	14	3	6	10	7
Relative standard deviation (%)	26	13	21	26	18

A FIB-SEM image of a cross section of the oxide layer was studied. The thickness was measured at several points ranging from 34 nm to 49 nm. As is the case for sample 1, the results show that the oxide thickness determined by GD-OES is correct within the statistical uncertainty, but it is not possible to say which of the two methods used in [Table D.3](#) is the more precise.

#### D.3.3 Results for sample 3 (13 RM 19 high-alloy steel)

Six laboratories participated, and two laboratories submitted DC/RF data. Eight results were reported.

In [Table D.4](#), the results are given for oxygen mass, oxygen mass fraction and oxide thickness. The oxide thickness given was evaluated directly from the graphs.

**Table D.4 — Results for sample 3**

	Oxygen mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxygen mass fraction %
No. of results	8	8	8
Average	11,0	4,5	45
Standard deviation	3,3	2,3	6
Relative standard deviation (%)	30,0	49,9	13

The average oxygen mass fraction determined is probably too high, but there is no validation method available to verify this.

In this case, the oxide thickness determined by GD-OES varied to such an extent that it is only possible to state that the order of magnitude is 5 nm. No independent validation measurements are available.

#### **D.3.4 Results for sample 4 (aluminium oxide on low-alloy steel)**

Five laboratories participated, and two laboratories submitted DC/RF data. Seven results were reported.

In [Table D.5](#), the oxide thickness is given both as read from the graphs (which are based on both methods described for estimating the density) and as calculated from the aluminium mass.

Two FIB-SEM images of a cross section of the oxide layer were studied. The thickness was measured at several points ranging from 250 nm to 350 nm. In the image from lab 1, two sublayers of the oxide were identified: a major layer 173 nm thick and a minor layer 73 nm thick. The oxide thickness determined by GD-OES is in the correct range and show good agreement with the FIB-SEM image.

**Table D.5 — Results for sample 4**

	Oxygen mass mg/m <sup>2</sup>	Aluminium mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxide thickness from Al mass nm	Oxygen mass fraction %
No. of results	7	7	7	7	7
Average	441	402	271	190	38
Standard deviation	167	156	115	74	15
Relative standard deviation (%)	38	39	42	39	40

#### **D.3.5 Results for sample 5 [titanium oxide on 18/8 high-alloy steel (blue)]**

Six laboratories participated, and two laboratories submitted DC/RF data. Eight results were reported.

In [Table D.6](#), the oxide thickness is given both as read from the graphs (which are based on both methods described for estimating the density) and as calculated from the titanium mass.

**Table D.6 — Results for sample 5**

	Oxygen mass mg/m <sup>2</sup>	Titanium mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxide thickness from Ti mass nm	Oxygen mass fraction %
No. of results	8	8	8	8	8
Average	151	113	70	43	45
Standard deviation	73	22	23	8	9

**Table D.6** (continued)

	<b>Oxygen mass</b> mg/m <sup>2</sup>	<b>Titanium mass</b> mg/m <sup>2</sup>	<b>Oxide thickness from graph</b> nm	<b>Oxide thickness from Ti mass</b> nm	<b>Oxygen mass fraction</b> %
Relative standard deviation (%)	48	19	33	19	21

A FIB-SEM image of a cross section of the oxide layer was studied. The thickness was measured at several points ranging from 43 nm to 63 nm. The results show that the oxide thickness determined by GD-OES is correct within the statistical uncertainty. In this case, it appears that the thickness determined from the titanium mass is in better agreement with the SEM image than that determined directly from the graphs.

### D.3.6 Results for sample 6 [titanium oxide on 18/8 high-alloy steel (green)]

Five laboratories participated.

In [Table D.7](#), the oxide thickness is given both as read from the graphs (which are based on both methods described for estimating the density) and as calculated from the titanium mass.

**Table D.7 — Results for sample 6**

	<b>Oxygen mass</b> mg/m <sup>2</sup>	<b>Titanium mass</b> mg/m <sup>2</sup>	<b>Oxide thickness from graph</b> nm	<b>Oxide thickness from Ti mass</b> nm	<b>Oxygen mass fraction</b> %
No. of results	5	5	5	5	5
Average	234	269	214	102	40
Standard deviation	107	112	123	42	11
Relative standard deviation (%)	46	42	18	42	28

In this case, the oxide thickness determined by GD-OES varied to such an extent that it is only possible to state that the order of magnitude is 100 nm. No independent validation measurements are available.

### D.3.7 Results for sample 7 (FeCrAl)

Five laboratories participated, and two laboratories submitted DC/RF data. Seven results were reported.

In [Table D.8](#), the results are given for oxygen mass, oxygen mass fraction and oxide thickness. The oxide thickness given was evaluated directly from the graphs.

**Table D.8 — Results for sample 7**

	<b>Oxygen mass</b> mg/m <sup>2</sup>	<b>Oxide thickness from graph</b> nm	<b>Oxygen mass fraction</b> %
No. of results	7	7	7
Average	13	5,6	41
Standard deviation	4	1,2	11
Relative standard deviation (%)	33	21	27

The average oxygen mass fraction determined is probably too high, but there is no validation method available to verify this.

In this case, the oxide thickness determined by GD-OES varied to such an extent that it is only possible to state that the order of magnitude is 5 nm. No independent validation measurements are available.

### D.3.8 Results for sample 8 (oxidized Si)

Four results were reported from four laboratories.

In [Table D.9](#), the results are given for oxygen mass, oxygen mass fraction and oxide thickness. The oxide thickness is given as evaluated directly from the graphs and as calculated from the Si mass.

**Table D.9 — Results for sample 8**

	Oxygen mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxide thickness from Si mass nm	Oxygen mass fraction %
No. of results	4	4	4	4
Average	288	253	246	45
Standard deviation	39	38	34	1
Relative standard deviation (%)	14	15	14	1

### D.3.9 Results for sample 9 (anodized aluminium)

Four results have been reported from four laboratories.

In [Table D.10](#), the results are given for oxygen mass, oxygen mass fraction and oxide thickness. The oxide thickness is given as evaluated directly from the graphs and as calculated from the Al mass.

**Table D.10 — Results for sample 9**

	Oxygen mass mg/m <sup>2</sup>	Oxide thickness from graph nm	Oxide thickness from oxygen mass nm	Oxygen mass fraction %
No. of results	4	4	4	4
Average	665	370	353	46
Standard deviation	75	39	40	3,9
Relative standard deviation (%)	11	13	11	8,6

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