TECHNICAL SPECIFICATION

ISO/TS 25138

First edition
2010-12-01

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 luminescente

---

PDF disclaimer

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

Adobe is a trademark of Adobe Systems Incorporated.

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

Contents

Page

Foreword

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

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

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

In other circumstances, particularly when there is an urgent market requirement for such documents, a technical committee may decide to publish other types of document:

— an ISO Publicly Available Specification (ISO/PAS) represents an agreement between technical experts in an ISO working group and is accepted for publication if it is approved by more than 50 % of the members of the parent committee casting a vote;

— an ISO Technical Specification (ISO/TS) represents an agreement between the members of a technical committee and is accepted for publication if it is approved by 2/3 of the members of the committee casting a vote.

An ISO/PAS or ISO/TS is reviewed after three years in order to decide whether it will be confirmed for a further three years, revised to become an International Standard, or withdrawn. If the ISO/PAS or ISO/TS is confirmed, it is reviewed again after a further three years, at which time it must either be transformed into an International Standard or be withdrawn.

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

ISO/TS 25138 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

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

1 Scope

This Technical Specification 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 and Al. Other elements that can be determined by the method are O, C, N, H, P and S.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 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 16962:2005, *Surface chemical analysis — Analysis of zinc- and/or aluminium-based metallic coatings by glow-discharge optical-emission spectrometry*

3 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 (depth profile).

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

1

4 Apparatus

4.1 Glow-discharge optical-emission spectrometer

4.1.1 General

The required instrumentation includes an optical-emission spectrometer system consisting of a Grimm type[1] or similar glow-discharge source (direct-current or radio-frequency powered) and a simultaneous optical spectrometer as described in ISO 14707, capable of providing suitable spectral lines for the analyte elements.

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 specimens, such as a metal block with circulating cooling liquid, is also recommended, but not strictly necessary for implementation of the method.

Since the principle of determination is based on continuous sputtering of the surface 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 500 measurements/second per spectral channel is recommended, but, for a large number of applications, speeds of > 50 measurements/second per spectral channel are acceptable.

4.1.2 Selection of spectral lines

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

4.1.3 Selection of glow-discharge source type

4.1.3.1 Anode size

Most GD-OES instruments on the market are delivered with options to use various anode diameters, 2 mm, 4 mm and 8 mm being the most common. Some older instruments have one anode only, usually 8 mm, while the most commonly used anode in modern instruments is 4 mm. A larger anode requires larger specimens and higher power during analysis; therefore the specimen is heated to a greater extent. On the other hand, a larger anode gives rise to a plasma of larger volume that emits more light, resulting in lower detection limits (i.e. higher analytical sensitivity). In a large number of applications, the 4 mm anode is a good compromise. However, in surface analysis applications it is rather common to encounter problems of overheating of the specimens due to e.g. surface layers of poor heat conductivity and/or very thin specimens. In such cases, the smaller 2 mm anode is preferable, even if there is some loss of analytical sensitivity.

4.1.3.2 Type of power supply

The glow-discharge source can be either a type powered by a direct-current (DC) power supply or a radio-frequency (RF) type. The most important difference is that the RF type can sputter both conductive and non-conductive specimens; hence this is the only type that can be used for 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.

4.1.3.3   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 Technical Specification 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[2][3] forms the basis for calibration and quantification as described in this Technical Specification. The emission yield has been found to vary with the current, the voltage and, to a lesser extent, the pressure[8]. It is impossible in practice to maintain all three parameters constant for all test specimens, due to variations in the electrical characteristics of different materials. In several instrument types, the electrical source parameters (the plasma impedance) can therefore be maintained constant by means of automatic systems that vary the pressure during analysis. Alternatively, there exist methods to correct for impedance variations by means of empirically derived functions[8], and this type of correction is implemented in the software of commercially available GD-OES systems.

5   Adjusting the glow-discharge spectrometer system settings

5.1   General

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

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

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

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

b)   good crater shape, for good depth resolution;

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

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

3

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.

5.2   Setting the parameters of a DC source

5.2.1   Constant applied current and voltage

5.2.1.1   General

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

5.2.1.2   Setting the high voltage of the detectors

Select test specimens with surface layers of all types to be determined. For all test specimens, run the source while observing the output signals from the detectors for the analyte atoms. Adjust the high voltage of the 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.

5.2.1.3   Adjusting the source parameters

For each type of test specimen, carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the 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 specimen surface layers; specimen cooling is beneficial in this regard.

5.2.1.4   Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a specimen with a metal oxide typical of the test specimens to be analysed to a depth of about 10 µm to 20 µm, but still inside the metal oxide. If no such specimen is available, use a brass specimen. Measure the crater shape by means of the profilometer device. Repeat this procedure a few times using slightly different values of one of the control parameters. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

5.2.2   Constant applied current and pressure

The two control parameters are the applied current and the pressure. Set the power supply for the glow-discharge source to constant-current operation. Then set the current to a typical value recommended by the manufacturer. If no recommended values are available, set the current to a value in the range 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range. Sputter a typical coated test specimen, and adjust the pressure until a voltage of approximately 700 V is attained in the metal oxide.

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the current and, if necessary, the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the pressure. These conditions are then used during calibration and analysis.

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

5.3   Setting the discharge parameters of an RF source

5.3.1   Constant applied power and pressure

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

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the applied power and, if necessary, the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the pressure.

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

5.3.2   Constant applied power and DC bias voltage

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

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the applied power and, if necessary, the DC bias voltage.

Optimize the crater shape as described in 5.2.1.4 by adjusting the DC bias voltage.

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

5.3.3   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 specimen in place but without plasma (vacuum conditions). The RF voltage is defined here as the RMS voltage at the coupling electrode.

Set the power supply for the glow-discharge source to constant effective power/constant RF voltage operation. First set the power to 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, 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 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the effective power and, if necessary, the RF voltage.

Optimize the crater shape as described in 5.2.1.4 by adjusting the RF voltage. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

5.4   Minimum performance requirements

5.4.1   General

It is desirable for the instrument to conform to the performance specifications given in 5.4.2 and 5.4.3 below.

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

5.4.2   Minimum repeatability

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

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

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

5.4.3   Detection limit

5.4.3.1   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 Technical Specification, 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.

5.4.3.2 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 specimen to be used as a blank. The composition of the specimen should preferably be similar, in terms of the elemental composition of the matrix, to that of the metal oxides to be analysed. Further, the specimen 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 specimens. For each measurement, the blank shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use an unsputtered area of the surface of the blank for each individual burn.

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

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

where

   DL   is the detection limit;

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

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

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

5.4.3.3 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 specimen 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 4.1.2) is to be used, the mass fraction of the analyte should preferably not exceed 1 %.

2   Perform three replicate burns on the chosen specimen. 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 specimens. For each measurement, the specimen shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use a freshly prepared area of the surface of the specimen for each individual burn. Average the three replicate emission intensities.

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

4 Calculate the detection limit using the following equation:

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

(2)

where

DL is the detection limit;

w_A is the mass fraction of the analyte in the specimen;

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

I_B is the average background intensity from step 3;

I is the average peak intensity from step 2.

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

6 Sampling

Carry out sampling in accordance with ISO 14284 and/or relevant national/international standards, as appropriate. If no such standards are available, follow the instructions from the manufacturer of the coated material or another appropriate procedure. The edges of a coated strip should preferably be avoided. The size of the test specimens taken shall be suitable for the glow-discharge source used. Typically, round or rectangular specimens with sizes (diameter, width and/or length) of 20 mm to 100 mm are suitable.

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

7 Calibration

7.1 General

Calibration of the system consists of determining, for each analyte and spectral line, the calibration equation 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 specimens. 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.

7.2 Calibration specimens

7.2.1 General

Whenever possible, spectrometric calibration specimens issued as CRMs (certified reference materials) shall be used. Due to the quantification being based on emission yields, the calibration specimens 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, specimens 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. The following considerations are the most important in the selection of the calibration specimens:

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

b) the specimens shall be homogeneous.

Based on these general requirements, the types of calibration specimen described in 7.2.2 to 7.2.13 are suggested. Additional calibration specimens of other alloy types containing the analytes may also be used.

NOTE 1   A reference material (RM) is a material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.

NOTE 2   A certified reference material (CRM) is a reference material, characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty and a statement of metrological traceability. By trademark, a Standard Reference Material® (SRM®) is a CRM issued by the National Institute of Standards and Technology, Gaithersburg, MD, USA.

7.2.2   Low-alloy iron or steel specimens

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

7.2.3   Stainless-steel specimens

Use stainless-steel specimens 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 %.

7.2.4   Nickel alloy specimens

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

7.2.5   Copper alloy specimens

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

7.2.6   Titanium alloy specimens

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

7.2.7   Silicon specimens

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

7.2.8   Aluminium alloy specimens

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

7.2.9 High-oxygen specimens

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

7.2.10 High-carbon specimens

Use cast-iron and/or tungsten carbide specimens with carbon mass fractions in the range 2 % to 10 %.

7.2.11 High-nitrogen specimens

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

7.2.12 High-hydrogen specimens

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

7.2.13 High-purity copper specimens

Use a high-purity copper specimen for which the total of the mass fractions of all other analytes is less than 0,001 %. This specimen can also be used to determine zero points for all analytes except copper.

7.3 Validation specimens

7.3.1 General

Validation (see 7.7) specimens shall be prepared in order to check the accuracy of the analytical results. The specimen types described in 7.3.2 to 7.3.6 are suggested, but other specimens may be used where appropriate. Note that these specimens can also be used as additional calibration specimens.

7.3.2 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_3O_4 making up the outer oxide layer. In some cases, these two phases are mixed throughout the oxide scale. The relative content of the two phases can be determined by XRD analysis. The thickness can be determined by optical microscopy.

7.3.3 Oxidized silicon wafers

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

7.3.4 TiN-coated specimens

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

7.3.5 Anodized Al_2O_3 specimens

Use metallic specimens with anodized Al_2O_3, the thickness of the anodized layer being as specified by the manufacturer.

7.3.6 TiO_2-coated specimens

Use metallic specimens coated with TiO_2, the thickness of the coating being as specified by the manufacturer.

7.4   Determination of the sputtering rate of calibration and validation specimens

The term "sputtering rate" is understood here to be equivalent to the mass loss rate during sputtering in the glow discharge. The term "relative sputtering rate" is understood here to be the sputtering rate of the specimen divided by the sputtering rate of a reference material sputtered under the same conditions. If the sputtered areas of the specimen and the reference specimen are the same, then the relative sputtering rate is equivalent to the relative sputtering rate per unit area. Proceed with sputtering rate determinations as follows:

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

b)   adjust the glow-discharge parameters to those selected in 5.2 or 5.3;

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

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

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

f)   for absolute sputtering rates:

   1)   measure the area of at least one crater,

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

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

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

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

g)   for relative sputtering rates:

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

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

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

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

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

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

NOTE 1   The sputtered mass can also be determined by weighing specimens before and after sputtering. However, this requires the use of scales of extremely high accuracy, and the uncertainty in such measurements is generally inferior to that with crater depth measurements.

11

NOTE 2   The sputtering rates of certain RMs might be available from the instrument manufacturer.

For calibration specimens in the form of oxide 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.

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

7.5   Emission intensity measurements of calibration specimens

The procedure for measuring the calibration specimens is as follows:

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

b)   Adjust the source parameter settings to those selected in 5.2 or 5.3. Choose a preburn time of 50 s to 200 s and a signal integration time of 5 s to 30 s.

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

7.6   Calculation of calibration equations

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[2]. 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 Technical Specification, no preference is given to a particular calculation method.

Depending on the type of source, the mode of operation and the calibration specimens chosen, the calibration equations for some elements might show a large separation between specimens 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 specimens which most resemble the specimens to be analysed.

7.7   Validation of the calibration

7.7.1   General

Carry out the following procedure immediately after calibration in order to confirm that the calibration equations are accurate. This process is called validation of calibration (see the Note). It is not necessary to

validate the calibration every time a new specimen is analysed. A related procedure (verification) shall be used on a more routine basis to check for instrument drift over time, as described in 7.8.

Two validation procedures are included in this clause. The first procedure (see 7.7.2) makes use of bulk reference materials and the second (see 7.7.3) employs metal oxide reference materials. Such metal oxide reference materials are often difficult to obtain. As a result, the validation procedure described in 7.7.3 is optional.

NOTE   Validation is the confirmation, through the provision of objective evidence, that the particular requirements for a specific intended use or application have been fulfilled (cited from ISO 9000:2005, 3.8.5). Validation of a method is defined in ISO/IEC 17025:2005, 5.4.5. Validation of the calibration is analogous to it (cf the Note in 7.8).

7.7.2 Checking analytical accuracy using bulk reference materials

a) Select, in accordance with 7.2, an appropriate number of bulk reference materials to be used for validation of the calibration.

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

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

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

7.7.3 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 glow-discharge 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 Technical Specification 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 9.2, the average mass fractions of the metal and oxygen for each validation specimen.

f) Compute, as described in 9.2.1 a) or 9.2.2 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 equations are acceptable.

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

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

7.8   Verification and drift correction

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

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

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

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

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

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

NOTE   Verification is the confirmation, through the provision of objective evidence, that specified requirements have been fulfilled (cited from ISO 9000:2005, 3.8.4; cf also the Note in 7.7.1).

8   Analysis of test specimens

8.1   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.

8.2   Setting of measuring time and data acquisition rate

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

As an example, suppose the specimen has a very thin 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.

8.3 Quantifying depth profiles of test specimens

Calculate quantified depth profiles, using the calibration equations established in accordance with Clause 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.

9 Expression of results

9.1 Expression of quantitative depth profile

An example of a quantitative depth profile is shown in Figure 1.

Key
X   depth (µm)
Y   mass fraction (%)
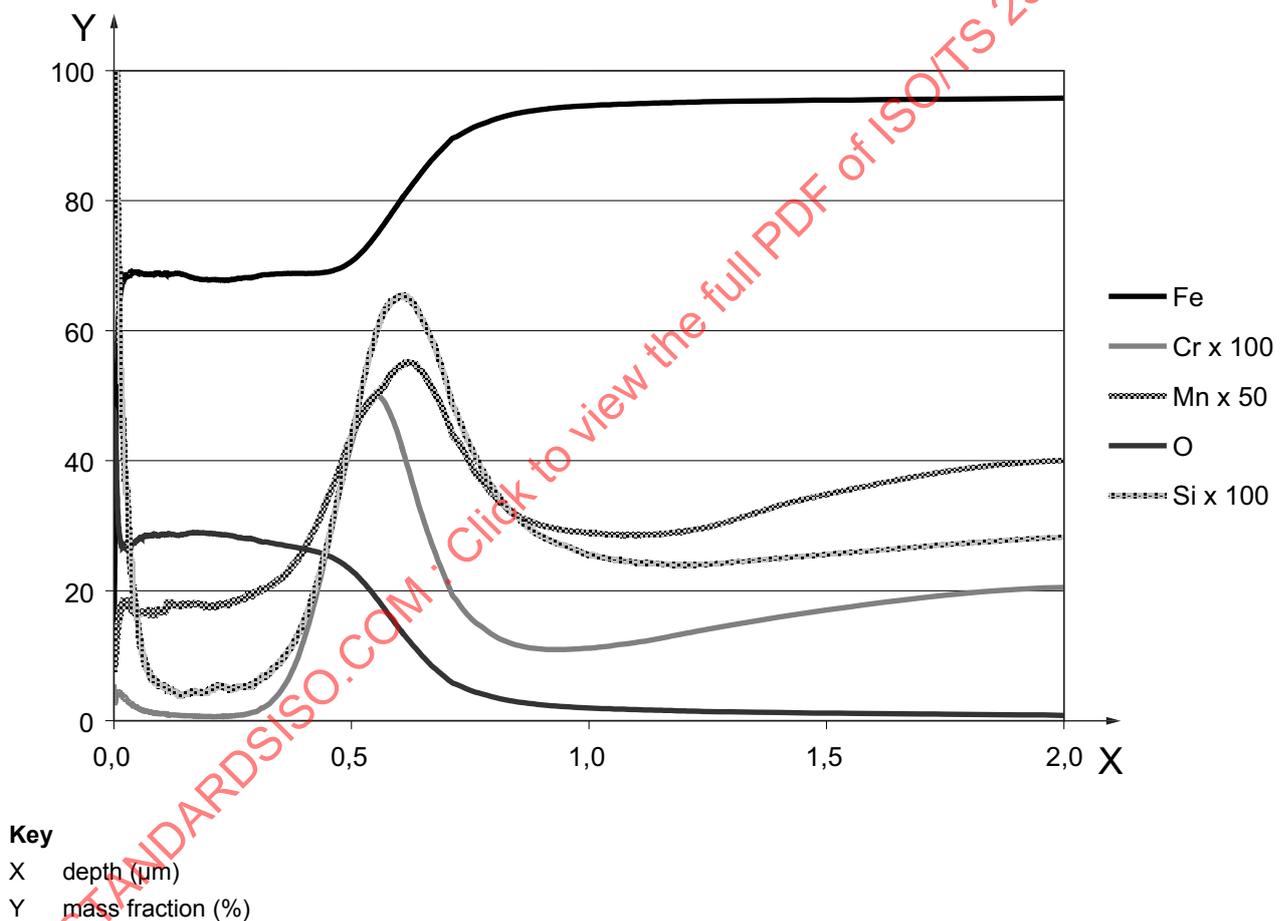
Figure 1 — Quantitative depth profile of an oxide on an annealed cold-rolled steel

9.2 Determination of metal oxide mass per unit area

9.2.1   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:

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 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.

9.2.2   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 16962:2005, 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 9.2.1 above.

c) Take as the integration depth the sum of the metal oxide thickness and the interface width.

9.2.3   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.

9.3   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 9.2) 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 16962:2005, Annex C, Clause C.2 (method 1).

10 Precision

An interlaboratory trial of this method was carried out by six laboratories, using nine specimens, each laboratory making two quantitative depth profiles of each specimen. The test specimens used are listed in Table D.1. The metal oxide thickness was determined as described in 9.2.1 a) and the oxygen mass fraction was determined as described in 9.3. 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 specimen.

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 specimens, 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 specimens for verification.

11 Test report

The test report shall include the following information:

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

b)   the laboratory and the date of the analysis;

c)   a reference to this Technical Specification;

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 Technical Specification, as well as of any optional operation, which may have influenced the results.

Annex A
(normative)

Calculation of calibration constants and quantitative evaluation of depth profiles

A.1 Symbols

A.1.1 Symbols used generally in this annex

A_{ij} atomic fraction of element i in segment j

A_D area of sputtering crater on specimen D

$I_{i\lambda}$ emission intensity at wavelength λ of element i

$I_{B\lambda}$ average background intensity at wavelength λ

m_{iDj} sputtered mass per unit area of element i in segment j of specimen D

m_{jtot} total sputtered mass per unit area in segment j

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

s_j current in segment j

s_0 reference current given by the instrument manufacturer

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

U_j voltage in segment j

U_0 threshold voltage for sputtering

U_D voltage recorded for calibration specimen D

U_{av} average voltage recorded for the set of calibration specimens used

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

w_{iD} mass fraction of element i in specimen D

w_{iDj} mass fraction of element i in depth segment j of specimen D

W_i atomic mass of element i

z_j thickness of segment j

Δt_j time increment corresponding to depth segment j

ρ_i density of pure element i

ρ_j density of segment j

A.1.2 Symbols used in Clauses A.2 and A.6 concerned with relative sputtering rates

B_λ spectral background term at wavelength λ, expressed as a mass fraction

$B_{\lambda\mathrm{rel}}$ related spectral background term at wavelength λ, expressed as a mass fraction

$e_{i\lambda}$ constant describing the degree of non-linearity for element i at spectral line λ

$k_{i\lambda}$ constant factor derived from the inverse emission yield (of element i at spectral line λ) divided by the relative sputtering rate

q_{D} sputtering rate, expressed as a mass loss rate per unit area, of specimen D

q_{ref} sputtering rate of a reference specimen (e.g. pure iron)

$q_{\mathrm{D}j}$ sputtering rate, expressed as a mass loss rate per unit area, in segment j of specimen D

$R_{i\lambda}$ inverse emission yield of element i at spectral line λ

$\mathscr{R}_{i\lambda}$ emission yield of element i at spectral line λ

A.1.3 Symbols used in Clauses A.3 and A.7 concerned with absolute sputtering rates

B'_λ spectral background term at wavelength λ, expressed as a mass fraction multiplied by the specimen sputtering rate

$B'_{\lambda\mathrm{rel}}$ related spectral background term at wavelength λ, expressed as a mass fraction

$e'_{i\lambda}$ constant describing the degree of non-linearity for element i at spectral line λ

$k'_{i\lambda}$ factor derived from the inverse emission yield divided by the sputtering rate

q'_{D} sputtering rate of specimen D

$q'_{\mathrm{D}j}$ sputtering rate in segment j of specimen D

$R'_{i\lambda}$ inverse emission yield of element i at spectral line λ

$\mathscr{R}'_{i\lambda}$ emission yield of element i at spectral line λ

A.2 Calculation of calibration constants using relative sputtering rates

Calibration is conducted using one of the following equations:

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

or

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

where

    $w_{i\mathrm{D}}$ is the mass fraction of element i in specimen D;

    $q_{\mathrm{D}}/q_{\mathrm{ref}}$ is the sputtering rate of specimen D relative to that of a reference specimen;

q_D is the sputtering rate expressed as the mass loss rate per unit area of specimen D;

q_{ref} is the sputtering rate expressed as the mass loss rate per unit area of a reference specimen;

$R_{i\lambda}$ is the inverse emission yield of element i at spectral line λ (see also Note 1);

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

B_λ is a spectral background term at wavelength λ;

$B_{\lambda rel}$ is a different but related spectral background term at wavelength λ which is expressed, in Equation (A.2), as a mass fraction and is often referred to as the "background equivalent concentration" (see also Note 2);

q_{ref}/q_D is equal to $1/(q_D/q_{ref})$ and is called the sputtering-rate correction factor.

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

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

where the emission yield is defined as

$$\mathscr{R}_{i\lambda} \equiv \left(I_{i\lambda} - I_{B\lambda}\right) / \left(w_{iD} \times q_D\right) \tag{A.4}$$

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

NOTE 2   The two spectral background terms are related by

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

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

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

and

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

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

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

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

The spectral background terms in Equations (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 equations:

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

or

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

where

w_{iD} is the mass fraction of element i in specimen D;

q'_D is the sputtering rate, expressed as the mass loss rate, of specimen D;

$R'_{i\lambda}$ is the inverse emission yield of element i at spectral line λ (see also Note 1);

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

B'_λ is a spectral background term at wavelength λ which may be treated as a constant or as a more complex function, expressed as a mass fraction multiplied by the specimen sputtering rate, provided by the manufacturer;

$B'_{\lambda\text{rel}}$ is a different but related spectral background term at wavelength λ which is expressed, in Equation (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, $\mathscr{R}'_{i\lambda}$, by

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

where the emission yield is defined as

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

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

NOTE 2   The two spectral background terms are related by

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

These equations 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, Equations (A.8) and (A.9) can be expressed, with such second-order terms, as shown in Equations (A.13) and (A.14), respectively:

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

and

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

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

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

The spectral background terms in Equations (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, λ, in segment j of the depth profile, calculate the corrected intensity, $I'_{i\lambda}$, using the equation

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

where

a_λ is a factor characteristic of spectral line λ;

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

s_j is the current in segment j;

s_0 is the reference current given by the instrument manufacturer.

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

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

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

A.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 equation

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

where

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

U_D is the voltage recorded for calibration specimen D;

U_{av} is the average voltage recorded for the set of calibration specimens used.

This type of equation 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

a) the source be operated at constant pressure;

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

c) a sufficient number of calibration specimens 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'_{ref}, of the reference specimen in accordance with

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

where

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

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

U_0 is the threshold voltage for sputtering.

The corrected sputtering rate of the reference specimen, q'_{ref}, is then inserted into Equations (A.20) and (A.22) below instead of q_{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, λ, of element i in segment j of the depth profile, calculate the corrected intensity, $I''_{i\lambda}$, using the equation

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

where

b_λ is a constant characteristic of spectral line λ;

I_H is the observed hydrogen emission intensity;

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

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

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

A.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 equation

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

where

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

I_HD is the hydrogen intensity recorded for calibration specimen D.

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

The requirements for implementing this hydrogen correction are that

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

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

NOTE   The regression parameter, $r^\text{H}_{i\lambda}$, 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 Equation (A.1) was used for calibration, carry out the following calculation steps.

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

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

$$\left(q_D/q_{ref}\right)_j = \sum_i \left[w_{iD} \times \left(q_D/q_{ref}\right)\right]_j \bigg/ 100 \tag{A.20}$$

The mass fraction, w_{iDj}, of element i in segment j of specimen D is given by the equation

$$w_{iDj} = \left[w_{iD} \times \left(q_D/q_{ref}\right)\right]_j \bigg/ \left(q_D/q_{ref}\right)_j \tag{A.21}$$

where w_{iDj} is expressed in percent.

The total sputtered mass per unit area, m_{jtot}, in segment j and in the corresponding time increment, Δt_j, is given by the equation

$$m_{jtot} = q_{ref} \times \left(q_D/q_{ref}\right)_j \times \Delta t_j \tag{A.22}$$

A.6.3 Calculation based on the mass fractions of the elements

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

Provided that the sum of all the elements determined constitutes > 98 % of the material analysed, the mass fraction, w_{iDj}, of element i in segment j of specimen D, expressed in percent, is given by the equation

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

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

NOTE   Equation (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 Equation (A.23) by the corresponding non-linear functions.

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

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

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

$$m_{iDj} = q_{Dj} \times w_{iDj} \times \Delta t_j / 100 \tag{A.25}$$

The total sputtered mass per unit area, m_{jtot}, in segment j is given by the equation

$$m_{jtot} = \sum_i m_{iDj} \tag{A.26}$$

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 Equation (A.8) was used for calibration, carry out the following calculation steps.

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

Provided that the sum of all the elements determined constitutes $> 98\,\%$ of the material analysed, calculate the sputtering rate, q'_{Dj}, of segment j of the depth profile of specimen D using the equation

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

The mass fraction, w_{iDj}, of element i in segment j of specimen D is given by the equation

$$w_{iDj} = \left(w_{iD} \times q'_{D} \right)_j \Big/ q'_{Dj} \tag{A.28}$$

where w_{iDj} is expressed in percent.

The total sputtered mass per unit area, m_{jtot}, in segment j and in the corresponding time increment, Δt_j, is given by the equation

$$m_{jtot} = q'_{Dj} \times \Delta t_j \Big/ A_D \tag{A.29}$$

where A_D is the area of the crater on specimen D.

A.7.3 Calculation based on mass fractions of the elements

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

Provided that the sum of all the elements determined constitutes > 98 % of the material analysed, calculate the mass fraction, w_{iDj}, of element i in segment j of specimen D, expressed as a mass fraction in percent, using the equation

$$w_{iDj} = \frac{\left(k'_{i\lambda} \times I_{i\lambda} - B'_\lambda\right)_j}{\sum\limits_i \left(k'_{i\lambda} \times I_{i\lambda} - B'_\lambda\right)_j} \times 100 \tag{A.30}$$

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

NOTE   Equation (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 Equation (A.30) by the corresponding non-linear functions.

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

$$q'_{Dj} = \sum\limits_i \left(k'_{i\lambda} \times I_{i\lambda} - B'_\lambda\right)/100 \tag{A.31}$$

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

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

The total sputtered mass per unit area, m_j, in segment j is given by the equation

$$m_j = \sum\limits_i m_{iDj} / A_D \tag{A.33}$$

A.8 Calculation of sputtered depth

A.8.1 General

The analytical method described in this Technical Specification 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 specimen D, calculate the density, ρ_j, using the equation

$$\rho_j = 100 / \sum\limits_i \frac{w_{iDj}}{\rho_i} \tag{A.34}$$

where ρ_i is the density of the pure element i.

For each segment, j, of the depth profile, calculate the thickness, z_j, of that segment using the equation

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

The total depth is determined by summing z_j over j using Equation (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 Δt_j.

If the density of the oxide is known from Annex C or another source, and the spectrometer software has provisions for manual input of the density, insert this value in Equation (A.35) in the time interval that the oxide is sputtered.

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

$$\rho_O = w_{ODj} \big/ \left(100 \big/ \rho_j - w_{iDj} \big/ \rho_i \right) \tag{A.36}$$

where

w_{ODj} is the mass fraction of oxygen in the oxide in segment j of specimen D;

ρ_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 specimen D;

ρ_i is the density of pure metal element i in the oxide.

Values of ρ_O for several oxides are given in Annex C. If the spectrometer software has provisions for manual input of density, insert the relevant value of ρ_O obtained from Equation (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 specimen D, calculate the atomic fraction, A_{ij}, of each element, i, using the equation

$$A_{ij} = \frac{\left(w_{iDj} / W_i \right)}{\sum_i \left(w_{iDj} / W_i \right)} \tag{A.37}$$

where W_i is the atomic mass of element i.

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

$$\rho_j = \sum_i A_{ij} \times \rho_i \tag{A.38}$$

For each segment, j, of the depth profile, calculate the thickness, z_j, using Equation (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	
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[a]	Self-absorption
Ni	225,386	0,01 to 100	
Ni	231,603	0,01 to 100	
Ni	341,78	0,001 to 100[a]	Weak self-absorption
Ni	349,30	0,005 to 100[a]	Weak self-absorption
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[a]	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	
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[a]	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	

[a] Use a non-linear calibration curve.