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Surface chemical analysis — General procedures for quantitative compositional depth profiling by glow discharge optical emission spectrometry

Analyse chimique des surfaces — Modes opératoires généraux pour le profilage en profondeur compositionnel quantitatif par spectrométrie d'émission optique à décharge luminescente

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Foreword

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

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

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

ISO 11505 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

Surface chemical analysis — General procedures for quantitative compositional depth profiling by glow discharge optical emission spectrometry

1 Scope

This International Standard describes a glow discharge optical emission spectrometric (GD-OES) method for the determination of the thickness, mass per unit area and chemical composition of surface layer films.

It is limited to a description of general procedures of quantification of GD-OES and is not applicable directly for the quantification of individual materials having various thicknesses and elements to be determined.

NOTE Any individual standard for a test material will have to specify a scope of a thickness of the surface layer as well as analyte elements, and include results of interlaboratory tests for validation of the methods.

2 Normative references

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

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

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

3 Principle

The analytical method described here involves the following processes:

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

b) excitation of the analyte atoms and ions in the plasma formed in the glow discharge device;

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

d) conversion of the qualitative 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.

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[10] 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. Sequential optical spectrometers (monochromators) are not suitable, since several analytical wavelengths must be measured simultaneously at high data acquisition speed.

The inner diameter of the hollow anode of the glow discharge source should be in the range 1 mm to 8 mm. A cooling device for thin specimens, such as a metal block with circulating cooling liquid, is also recommended, but not strictly necessary for implementation of the method.

Since the principle of determination is based on continuous sputtering of the surface layer, the spectrometer shall be equipped with a digital readout system for time-resolved measurement of the emission intensities. A system capable of a data acquisition speed of at least 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 nonlinear 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, as 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, with 2 mm, 4 mm and 8 mm being the most common. Some older instruments have one anode only, usually 8 mm, while the most commonly used anode in modern instruments is 4 mm. A larger anode requires larger specimens and higher power during analysis; therefore the specimen is heated to a greater extent. On the other hand, a larger anode gives rise to a plasma of larger volume that emits more light, resulting in lower detection limits (i.e. higher analytical sensitivity). Furthermore, a larger anode helps to mask inhomogeneity within a surface layer. This may or may not be an advantage, depending on the application. In a large number of applications, the 4 mm anode is a good compromise. However, in surface analysis applications it is rather common to encounter problems of overheating of the specimens due to, 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 also exist. 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 that 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 International Standard 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[11][12] forms the basis for calibration and quantification as described in this International Standard. The emission yield has been found to vary with the current, the voltage and, to a lesser extent, the pressure[17]. 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[17], 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.

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 10–100 W, but it must be noted that the RF power losses in connectors, cables, etc. vary considerably between different instrument models. Typical power losses are in the range 10–50 % 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.

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.

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 5.2 and 5.3.

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

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

5.2 Setting the discharge 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 of 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 discharge parameters

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

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

5.2.1.4 Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a specimen with a surface layer typical of the test specimens to be analysed to a depth of about 10 µm to 20 µm, but still inside the surface layer. This is only possible for applications where surface layers of such thickness are available. If no such specimen is available, use a steel or brass specimen. Measure the crater shape by means of the profilometer device. Repeat this procedure a few times using slightly different values of one of the control parameters. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis, provided that the stability of the emission conditions obtained in step 5.1.1.3 is not compromised. In some cases, there is a certain trade-off between these two requirements.

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 of 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range. Sputter a typical coated test specimen, and adjust the pressure until a voltage of approximately 700 V is attained in the surface layer.

Set the high voltage of the detectors as described in 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 control parameters. These conditions are then used during calibration and analysis.

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.

5.2.2.1 Constant applied voltage and pressure

The two control parameters are applied voltage and pressure. Set the power supply for the glow discharge source to constant voltage operation. First set the voltage to a typical value recommended by the manufacturer. If no recommended values are available, set the voltage to 700 V. Sputter a typical coated test sample, and adjust the pressure until a current is attained in the range of 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 5.2.1.2.

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

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

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.

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

Set the high voltage of the detectors as described in 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 control parameters.

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. Note that this procedure is only applicable to conducting surface layers, since the DC bias voltage cannot be measured for a specimen with a non-conducting surface layer.

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 control parameters.

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 (see note below).

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 of 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 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 control parameters. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

NOTE In order to determine the RF RMS voltage it is essential to include the offset caused by the DC bias voltage, which is not possible to measure at the coupling electrode when non-conductors are sputtered. However, when only thin (<100 µm) non-conductive layers on a conductive specimen are analysed, the offset can be estimated and the amplitude of the RF voltage multiplied by 1,22 can be used as a good estimate of the RMS voltage[18]. For thick non-conductors more complex calculations must be carried out[19]. However, analysis of thick non-conductors is outside the scope of this International Standard.

5.4 Minimum performance requirements

5.4.1 General

The instrument needs 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 International Standard.

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 50 s and a data acquisition time in the range 5 s to 30 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 surface layers considered here. For the purposes of this International Standard, the detection limit for each analyte will be acceptable if it is equal to or less than one-fifth of the lowest expected mass fraction in the surface layer to be analysed.

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 to be performed.

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

b) Perform 10 replicate burns on the blank. For each burn, acquire the emission intensity at the analytical wavelength for 10 s. These are the background emission intensity measurements. The glow discharge conditions used should preferably be the same as those that will be used in the analysis of the coated specimens. For each measurement, the blank shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use an unsputtered area of the surface of the blank for each individual burn.

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

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

where

DL is the detection limit;

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

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

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

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, performed as follows.

a) Select a bulk specimen which has a matrix composition that is similar to that of the surface layers to be analysed and in which the mass fraction of the analyte is greater than 0,1 % and accurately known. If an analytical transition that is prone to self-absorption (see 4.1.2) is to be used, the mass fraction of the analyte should preferably not exceed 1 %.

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

c) Select a peak-free region of the emission spectrum within 0,2 nm of the analytical peak. Perform 10 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 10 replicate measurements.

d) Calculate the detection limit using the following equation:

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

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. This is due to the fact that diameter of the sealing O-ring of the source typically is in the range 8–20 mm, and it is desirable to have sufficient area to make at least two replicate measurements on each specimen.

Rinse the surface of the specimen with an appropriate solvent (e.g. 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 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.3 or Clause A.4. 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, but RMs (reference materials) are also acceptable. Due to the quantification being based on emission yields, the calibration specimens need not be very similar to the surface layer 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 are valuable for the determination of the spectral backgrounds. The following considerations are the most important in the selection of the calibration specimens:

a) it is recommended to use at least five calibration specimens for each analyte, covering a range from zero to the highest mass fraction to be determined;

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

Based on these general provisions, the types of calibration specimen described in 7.2.2 to 7.2.7 are suggested. Additional calibration specimens of other alloy types containing the analytes of interest for the intended applications 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. A standard reference Material (SRM) is a CRM issued by NIST, the US National Institute of Standards and Technology.

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 with sufficient accuracy by subtracting the sum of the mass fractions for all other known elements from 100 %. Note that if any significant impurities are not measured then the calculated iron mass fraction will be higher than the true value. Low alloy steel is recommended because there is an abundance of such CRM's available, and they are often certified for a large number of elements.

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 %, in such a composition that leave Fe at > 30 %. Stainless steel is recommended because there is an abundance of such CRMs available, and they are often certified for a large number of elements

7.2.4 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.

7.2.5 High-carbon specimens

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

7.2.6 High-nitrogen specimens

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

7.2.7 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.

7.2.8 High-purity zinc specimens

Use a high-purity zinc specimen for which the total of the mass fractions of all other analytes is less than 0,001 %. This specimen is mainly to be used to determine zero points for all analytes except zinc. It is suitable for this purpose due to the fact that zinc has an emission spectrum with very few spectral lines.

7.3 Validation specimens

Validation (see 7.7) specimens shall be prepared in order to check the accuracy of the analytical results. These specimens can also be used as additional calibration specimens.

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 by following the procedure 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 or by means of a full 3D measurement if the device used has this capability[17].

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, and

   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 averaged 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 (A low-alloy steel, e.g. NIST 1761, is recommended for a multi-matrix method since the sputtering rate is intermediate, but for a more matrix-matched method

a better suited specimen can be used) 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, and

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. In several cases, it is a more practical method than the one described above. However, this requires the use of scales of extremely high accuracy, and the uncertainty in such measurements is generally inferior to that with crater depth measurements.

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

If laboratory means are available, measure the density of each calibration specimen. A suitable method for homogeneous specimens is specimen mass divided by specimen volume, where the specimen volume is measured by immersion of the specimen in water following the method of Archimedes (see ISO 3369). Alternatively, the specimen volume can be estimated from the specimen dimensions or the density calculated from the specimen composition as described in Annex A [see Formula (A.34)].

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 blow the surface dry with a stream of inert gas (argon or nitrogen) or clean, oil-free air, being careful not to touch the 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 Annex A. The software for all commercially available GD-OES instruments incorporates at least one of these calculation methods.

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 described below. The first procedure (see 7.7.2) makes use of bulk reference materials and the second (see 7.7.3) employs surface layer reference materials. Such surface layer reference materials are often difficult to obtain. As a result, the validation procedure described in 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 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 surface layer 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 surface layer reference material for a sufficiently long time to ensure that the surface layer is completely removed and sputtering has continued well into the substrate.

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

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

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

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

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

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 surface layers of the specimens. It should be remembered that a very high rate results in very short integration times, leading to more noisy signals. As a general recommendation, a layer or other feature in the depth profile should include at least 10 data points. It is often advisable to have a subdivision of at least two time intervals, using a high acquisition rate initially in order to resolve rapidly changing features in the top surface layer, then to decrease the rate in order to improve the signal-to-noise ratio of the signals.

As an example, suppose the specimen has a very thin surface layer of thickness 5 nm and the sputtering rate is 50 nm/s. It is advisable to maintain a high acquisition rate to a depth at least twice the layer thickness, in this case 10 nm. This means maintaining a high acquisition rate for at least 0,2 s and collecting at least 20 data points during this time. This means that the minimum initial data acquisition rate has to be 100 measurements per 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.

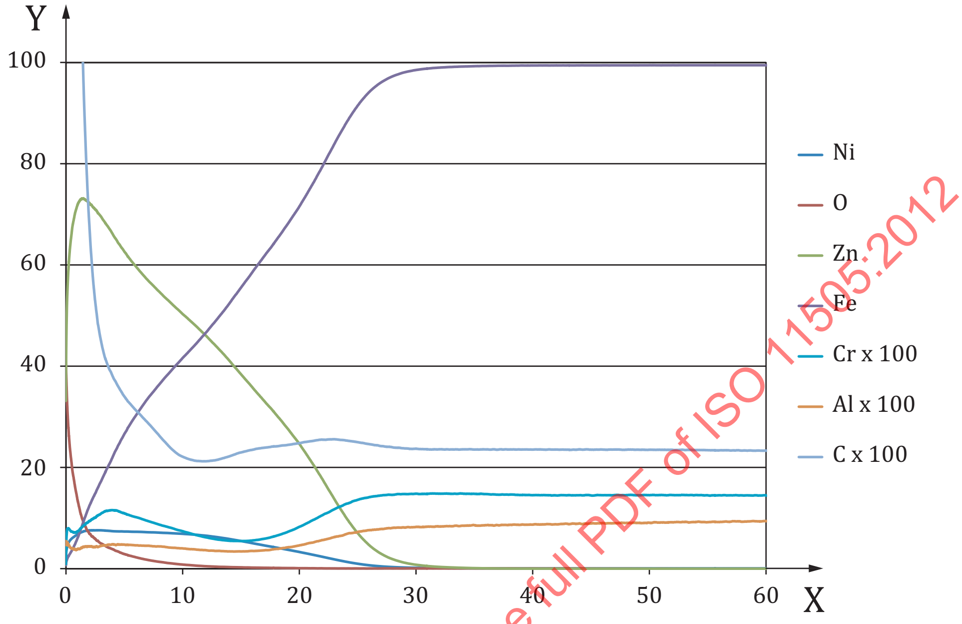
8.3 Quantifying depth profiles of test specimens

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.

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 annealed ZnNi coating on steel

9.2 Determination of total coating mass per unit area

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

The following is a general recommendation for determination of the integration depth.

a) Define the surface layer thickness as the distance from the surface to the depth at which the mass fraction of a selected major surface layer element is reduced to 50 % of the “plateau” value in the surface layer.

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

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

9.2.2 In cases where a major element of the surface layer is the same as that of the substrate (e.g. iron oxide on a steel substrate), there exist special calculation methods for certain applications, e.g. ZnFe on steel described in ISO 16962.

9.3 Determination of average mass fractions

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

10 Precision

Due to a lack of sufficient quantity of specimens with surface coatings of sufficiently uniform thickness, the precision of the method has not been determined. However, it is anticipated that precision tests for specific applications will be carried out.

11 Test report

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

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

b) the laboratory and the date of the analysis;

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

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

e) any unusual features noted during the determination;

f) any operation not specified in this International Standard or any optional operation which may have influenced the results.

Annex A

(normative)

Calculation of calibration constants and quantitative evaluation of depth profiles

A.1 General

All methods for calibration and quantitative evaluation of depth profiles in commercially available spectrometer systems shall be based on the concept of *emission yield* (EY), which can be defined as the emitted light of a spectral line per unit sputtered mass of the corresponding element[11][12]. The EY is an element- and instrument-dependent quantity, which must be determined independently for each spectral line and instrument. The assumption which forms the basis for this quantification technique is that the integrated signal intensity from one element (and spectral line) is proportional to just the sputtered mass of that element, which implies that the EY is independent of the sample composition (matrix). This has been investigated by several authors[13][14] and is by now widely accepted to be valid, at least to a first approximation. A few different mathematical models for calibration and quantification of intensity depth profiles have been developed based on the matrix-independent EY concept, therefore the calculation steps in the software of different commercially available instruments are not identical. Furthermore, there exist a few types of correction algorithms for variations in the source discharge parameters, based on empirical models. More recently, correction algorithms for the influence of hydrogen on the EY have also been developed and incorporated in the software of commercial instruments. In the following, all known varieties of these quantification calculations are described in detail. It must be emphasized that they are all valid and acceptable for the purpose of this standard, the relevant test of validity in an actual spectrometer system is the validation procedure described in section 7.7. Any further development of quantification calculations will also be acceptable provided these validation procedures give satisfactory results.

A.2 Symbols

A.2.1 Symbols used generally in Annex A

A_{ij}	atomic fraction of element *i* in depth segment *j*
A_D	area of sputtering crater on specimen D
a_λ	constant describing the influence of current on the intensity of spectral line λ
b_λ	constant describing the influence of hydrogen on the intensity of spectral line λ
$I_{i\lambda}$	emission intensity of element *i* at wavelength λ
$I'_{i\lambda}$	corrected emission intensity of element *i* at wavelength λ
$I''_{i\lambda}$	corrected emission intensity of $I'_{i\lambda}$
I_H	observed hydrogen emission intensity
I_{Href}	hydrogen emission intensity from a reference material, e.g. a TiH_2 layer or a specific type of polymer.
I_{HD}	hydrogen intensity recorded for calibration specimen D

$I_{\mathrm{B}\lambda}$	average spectral background intensity at wavelength λ
q_{ref}	sputtering rate of a reference specimen (e.g. pure iron)
q'_{ref}	corrected sputtering rate of a reference specimen (e.g. pure iron)
$m_{i\mathrm{D}j}$	sputtered mass per unit area of element *i* in depth segment *j* of specimen D
$m_{j\mathrm{tot}}$	total sputtered mass per unit area in depth segment *j*
$r_{i\lambda}^{U}$	regression parameter in the calibration function
s_j	current in depth 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 depth segment *j*
U_0	threshold voltage for sputtering
U_{D}	voltage recorded for calibration specimen D
U_{av}	average voltage recorded for the set of calibration specimens used
U_{cal}	voltage used for the calibration of the method
$w_{i\mathrm{D}}$	mass fraction of element *i* in specimen D
$w_{i\mathrm{D}j}$	mass fraction of element *i* in depth segment *j* of specimen D
W_i	atomic mass of element *i*
z_j	thickness of depth segment *j*
Δt_j	time increment corresponding to depth segment *j*
ρ_i	density of pure element *i*
ρ_j	density of depth segment *j*

A.2.2 Symbols used in Clauses A.3 and A.7 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 depth segment j of specimen D
$R_{i\lambda}$	inverse normalized emission yield of element i at spectral line λ
$R''_{i\lambda}$	corrected inverse normalized emission yield of element i at spectral line λ
$\mathfrak{R}_{i\lambda}$	Normalized emission yield of element i at spectral line λ

A.2.3 Symbols used in Clauses A.4 and A.8 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, expressed as mass loss rate, in depth segment j of specimen D
$R'_{i\lambda}$	inverse emission yield of element i at spectral line λ
$\mathfrak{R}'_{i\lambda}$	emission yield of element i at spectral line λ
$r^\mathrm{H}_{i\lambda}$	a regression parameter describing the influence of hydrogen on spectral line λ

A.3 Calculation of calibration constants using relative sputtering rates

Calibration shall be conducted using one of the following equations:

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

or

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

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

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

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

where the emission yield is defined as

$$\mathfrak{R}_{i\lambda} \equiv (I_{i\lambda} - I_{\mathrm{B}\lambda}) / (w_{i\mathrm{D}} \times q_\mathrm{D}) \qquad \text{(A.4)}$$

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

NOTE 2 The two spectral background terms are related by

$$B_{\lambda\mathrm{rel}} = (q_\mathrm{ref}/q_\mathrm{D}) \times B_\lambda \qquad \text{(A.5)}$$

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

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

and

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

where $e_{i\lambda}$ is a constant describing the degree of nonlinearity for element *i* at spectral line λ.

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

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

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

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

A.4 Calculation of calibration constants using absolute sputtering rates

Calibration is conducted using one of the following equations:

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

or

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

where

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

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

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

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

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

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

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

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

where the emission yield is defined as

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

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

NOTE 2 The two spectral background terms are related by

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

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

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

and

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

where $e'_{i\lambda}$ is a constant describing the degree of nonlinearity for element i at spectral line λ.

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

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

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

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

A.5.1 General

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

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

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

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

where

$I'_{i\lambda}$ is corrected emission intensity of element i at wavelength λ;

a_λ is a factor characteristic of spectral line λ;

$f(U_j)$ is the value in depth 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 depth segment j;

s_0 is the reference current given by the instrument manufacturer.

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

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

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

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

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

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

where

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

$r^U_{i\lambda}$ 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 needs to be added to those described below.

The requirements for implementing the voltage correction are that

a) the source be operated at constant pressure;

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

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.5.4 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

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

where

q'_{ref}	is corrected sputtering rate of a reference specimen (e.g. pure iron);
s_j	is current in depth segment *j*;
s_{cal}	is the current used for the calibration of the method;
U_j	is voltage in depth segment *j*;
U_{cal}	is the voltage used for the calibration of the method;
U_0	is the threshold voltage for sputtering.

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

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

A.6.1 General

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

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

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

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

where

$I'_{i\lambda}$ is corrected emission intensity of element *i* at wavelenght λ;

$I''_{i\lambda}$ is corrected emission intensity of $I'_{i\lambda}$;

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 to A.7.

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

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

A multiplicative correction of the emission yield for hydrogen is inserted in the calibration function in accordance with the equation

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

where

$R''_{i\lambda}$ is the corrected inverse emission yield of element *i* at spectral line λ;

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

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

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

A.7.1 General

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

A.7.2 Calculation based on the relative elemental sputtering rate

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

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

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

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

where

$(q_\mathrm{D}/q_\mathrm{ref})_j$	is the relative sputtering rate of segment *j* of the depth profile of specimen D;
$w_{i\mathrm{D}}$	is the mass fraction of element i in specimen D.

The mass fraction, $w_{i\mathrm{D}}$, in the Formula (A.20) is interpreted as $w_{i\mathrm{D}j}$, of element *i* in depth segment *j* of specimen D and given by the equation

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

where

$w_{i\mathrm{D}j}$	is expressed in percent;
$(q_\mathrm{D}/q_\mathrm{ref})$	in Formulae (A.20) and (A.21) are interpreted as $(q_\mathrm{D}/q_\mathrm{ref})$ *j* of the sputtering rate in depth segment *j* of specimen D relative to that of a reference specimen.

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

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

where

q_ref	is the sputtering rate expressed as the mass loss rate per unit area of a reference specimen;
$(q_\mathrm{D}/q_\mathrm{ref})_j$	is the sputtering rate in depth segment *j* of specimen D relative to that of a reference specimen derived by (A.20).

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

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