

Surface chemical analysis – Determination of thickness and chemical composition of zinc-based metallic coatings by glow discharge optical emission spectrometry

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Foreword

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

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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. This International Standard was developed by ISO/TC 201 *Surface Chemical analysis*.

4 Apparatus

4.1 Glow discharge optical emission spectrometer

4.1.1 General

An optical emission spectrometer equipped with a Grimm type (1) or similar glow discharge source (direct current or radio frequency powered) and a direct reading optical spectrometer, incorporating suitable spectral lines for the analyte elements (see table 1 for recommended lines).

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

The glow discharge optical emission spectrometer will be satisfactory if the limits of detection are in reasonable agreement with the values given by the manufacturer and it meets the precision criteria given in 4.1.1 to 4.1.2. It is also desirable that the instrument should conform to the additional performance requirements given in 4.1.3

4.1.2 Minimum repeatability

Perform 10 measurements of the emission intensity on a homogeneous bulk sample with a content of the analyte exceeding 1% by mass. Allow the discharge at least 60 s stabilisation time (often referred to as preburn) before each intensity measurement. Each measurement shall be located on a newly prepared surface of the sample. Calculate the standard deviation of the 10 measurements. The standard deviation should not exceed 2% of the mean intensity of the analyte. If this is the case, there is probably some malfunction and the instrument should be serviced before further use.

4.1.3 Limit of detection

The limit of detection is defined as three times the standard deviation of 10 measurements of the background emission intensity performed on a sample with zero content of the analyte, divided by the sensitivity expressed as (intensity/mass fraction).

It should be noted that according to the definition above, the limits of detection for all analytes are matrix-dependent, mainly due to the fact that the spectral background intensity varies with the matrix. Consequently, the limit of detection cannot be uniquely determined for the full range of different zinc based alloys within the scope of this standard.

The limit of detection should be measured using a sample which contains similar matrix elements in concentrations as

close as possible to those found in the coating types to be determined. The limit of detection should preferably be smaller than one tenth of the minimum content of the measured analyte.

4.2 Data acquisition

Since the principle of determination is based on continuous sputtering of the surface coating, the spectrometer shall be equipped with a digital readout system for time-resolved measurement of the emission intensities. A system with capability for data acquisition speed of at least 500 measurements/second is recommended, but for the applications within the scope of this standard a speed of 2 to 100 measurements/second is acceptable.

5 Sampling

Carry out sampling in accordance with ISO 14284 and appropriate national/international standards and, if appropriate standard is not available, the recommendations of the manufacturer of the coated material. In general, the edges of a coated strip should be avoided. The size of the test samples should be suitable for the glow discharge source used. Typically, round or rectangular samples with sizes (diameter, width and/or length) of 20 - 100 mm are suitable.

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

6 Procedure

6.1 Selection of spectral lines

For each analyte to be determined, there exist a number of spectral lines which can be used. Suitable lines shall be selected on the basis of several factors including the spectral range of the spectrometer used, analyte concentration range, sensitivity of the spectral lines and spectral interference from other elements present in the samples. In this type of application, where most of the analytes of interest are major elements in the samples, special attention shall be paid to the occurrence of self-absorption (sometimes referred to as self-reversal) of certain highly sensitive spectral lines (so-called resonance lines). Self-absorption causes non-linear calibration curves at high analyte concentration levels, and strongly self-absorbed lines should therefore be avoided for the determination of majors. In table 1, some recommendations concerning suitable spectral lines are given.

Table 1 — Recommended spectral lines for determination of given elements

Element	Wavelength (nm)	Estimated useful Concentration range % by mass	Comments
Zn	330,26	0,001 to 100	
Zn	334,50	0,001 to 100	
Zn	481,053	0,001 to 100	
Al	172,50	0,1 to 100	
Al	396,15	0,001 to 100*	Self-absorption
Ni	231,603	0,01 to 100	
Ni	341,78	0,001 to 100*	Weak self-absorption
Ni	349,30	0,005 to 100*	Weak self-absorption
Pb	202,20	0,001 to 10	
Pb	405,87	0,01 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*	Weak self-absorption
Fe	379,50	0,01 to 100	
Cu	296,12	0,01 to 100	
Cu	327,40	0,001 to 5	Strong self-absorption

* Use non-linear calibration curve

6.2 Optimising the glow discharge spectrometer settings

6.2.1 General

Follow the manufacturer's instructions for preparing the instrument for use. In particular, check that the entrance slit to the spectrometer is correctly adjusted, following the procedure given by the instrument manufacturer. This ensures that the emission intensities are measured on the peaks of the spectral lines for optimal signal to background ratio.

6.2.2 Setting the discharge parameters of a DC source

Set the power supply for the glow discharge source to constant current operation. Depending on the sample type and cooling system, the maximum allowable current, voltage and power varies. Select the current to a value in the range 15 mA to 30 mA for a 4 mm anode, 40 mA to 100 mA for a 7 mm or 8 mm anode. For other anode diameters, set the current to a value which gives a current density at the sample surface in the range 0,8 mA to 2 mA/mm². If no beforehand knowledge about the optimum current is at hand, it is recommended to start with a value somewhere in the middle of the recommended range

If the spectrometer is equipped with a system for active pressure regulation of the glow discharge, set the voltage to a fixed value in the range 400 V to 1000V. If no beforehand knowledge about the optimum voltage is at hand, it s

recommended to set the voltage to 600V for the first trials.

An active pressure regulation system is preferable. If the spectrometer is not equipped in this way, the pressure shall be adjusted manually for each sample type until the voltage reaches the desired value within a 5% tolerance. Select test samples with coatings of all types to be determined. Using these samples, run the source while observing the output signals from the detectors for the analyte atoms. Adjust the high voltage of the detectors in such a way that sufficient sensitivity at the lowest analyte concentrations is ensured, without saturation of the detector system at the highest analyte concentrations.

For each test sample, carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the coating completely and 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 signals from the analytes throughout the depth profile. If this is found not to be the case, reduce the discharge current by a small amount, readjust the pressure to obtain the previously selected discharge voltage, and sputter through the coating of the same sample again. If the results are still unsatisfactory, reduce the voltage by a small amount and repeat the measurement. If found necessary, repeat this procedure for a number of current-voltage combinations until stable discharge conditions are obtained.

When stable discharge conditions have been obtained, record a few depth profiles (4 – 8) with voltage-current combinations slightly varied in such a way as to maintain approximately the same electrical power. Observe the transition zone in the depth profiles between coating and substrate. Select conditions that give the sharpest depth profile, i.e. where the intensity of the major coating elements drops from 85% of the maximum intensity to 15% in the shortest time interval relative to the total sputtering time through the coating.

6.2.3 Setting the discharge parameters of an RF source

In the same way as in DC systems, the RF source parameters must be chosen here to achieve three aims: adequate sputtering of the sample, good crater shape for good depth resolution and constant excitation conditions in calibration and analysis. Unlike the DC source, the applied electrical power in a RF source is not equivalent to the effective plasma power in the glow discharge. Substantial power losses are incurred in the source and the sample, and these losses vary in a rather complex way that is different for each source type. As a consequence, it is generally not possible to measure and control the electrical parameters of a RF plasma in the same way as a DC plasma. Currently most RF sources are operated with constant applied power and constant pressure. Other modes also exist such as; constant applied voltage and constant pressure; or constant effective power and applied voltage. These modes are likely to become more common in the future.

All RF operational modes are allowed in this standard provided they meet the above mentioned three aims. It will be assumed in the following description that the source is being operated with constant applied power and pressure but the description is readily conformable to other modes of operation.

First set the applied power and pressure to typical values recommended by the manufacturer of the instrument, for example, 35W and 7hPa. Measure the penetration rate (i.e. depth per unit time) on an iron or steel sample. The power should be adjusted to give a penetration rate of about 3 $\mu\text{m}/\text{min}$. Next sputter one of the brass samples to a depth of about 20 μm and measure the crater shape by means of a suitable profilometer device. Repeat this procedure on the brass sample using different pressure settings until an optimally flat bottomed crater is achieved. Re-measure the penetration rate on the iron or steel sample and adjust the power if necessary to return to about 3 $\mu\text{m}/\text{min}$. Repeat the cycles of power and pressure adjustment until no significant change is noted in the penetration rate or crater shape. Note the power and pressure used in units provided by the instrument. These conditions are then used during calibration and analysis.

If the RF source can be operated in the constant effective power and constant applied voltage mode, this is functionally equivalent to the constant current and constant voltage mode normally used in DC systems. This means that the setting of the discharge parameters can follow the procedure in 6.2.2.

6.2.4 Preliminary precision test

Select a few suitable bulk calibration samples (see 6.3.1) and evaluate the criteria according to 4.1.1. Ensure that the current and voltage settings used are the same as those selected for the coated materials.

6.3 Calibration

6.3.1 General

Calibration of the system consists of determining, for each analyte and spectral line, a quantity known as the emission yield (2.3.4) which is defined as the integrated emission intensity per unit mass of the analyte. The principle of quantification used in this standard is based on the observation that the emission yield is a matrix-independent quantity, or at least very nearly so (3.5). In order to determine the emission yield, it is necessary to know both the chemical composition and the sputtering rates (mass loss rate) of the calibration samples.

6.3.2 Calibration samples

Whenever possible, spectrometric calibration samples issued as CRMs (Certified Reference Materials) should be used. Due to the quantification being based on emission yields, the calibration samples need not be very similar to the coating materials in composition but shall have sputtering rates, which are well determined and reproducible. In particular pure or nearly pure zinc samples is not recommended, due to difficulties in obtaining reproducible and stable sputtering rates in zinc. Furthermore, high purity metals are not necessary in order to calibrate correctly for high concentrations, but they are valuable for the determination of the spectral backgrounds. The following considerations are the most important in the selection of the calibration samples:

- a) there shall be at least 5 calibration samples for each analyte; covering a range from zero to the highest concentrations to be determined;
- b) the samples shall be homogeneous;
- c) the samples shall have well determined sputtering rates.

Based on these general recommendations, the following types of calibration samples are suggested. It should be noted that these recommendations constitute a minimum requirement, and additional calibration samples of other alloy types containing the analytes may be used.

Brass calibration samples

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

ZnAl alloy samples

Select at least two ZnAl alloy samples with a zinc content of 40 % by mass to 95 % by mass.

Low alloy iron or steel samples

Select at least two low alloy iron or steel with concentration of iron greater than 98%(m/m). The iron content may be determined by subtracting the sum of the contents for all other known elements from 100%(m/m).

Stainless steel samples

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

Nickel based alloy samples

Select at least one nickel based alloy sample with a nickel content of more than 70 % by mass.

Aluminium to silicon alloy samples

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

High purity copper sample

Select a high purity copper sample with concentrations of the analytes less than 0,01 % by mass. This sample can be used as zero points for all analytes except copper, even if the exact concentrations of the analytes are not known.

Zinc-nickel electric coated RMs

Select at least one electric coated RM with less than 20%(m/m) nickel for validation of calibration graph. Thickness and chemical compositions shall be determined by referee methods specified by such as ISO *****(to be published).

Zinc-iron coated RMs

Select at least one electric coated RM with more than 30%(m/m) zinc and more than 5% (m/m) iron for validation of calibration graph. Thickness and chemical compositions shall be determined by referee methods specified by such as ISO *****(to be published).

Zinc-aluminium coated RMs

Select at least one zinc- aluminium coated RM with more than 10%(m/m) zinc and more than 5%(m/m) aluminium for validation of calibration graph. Thickness and chemical compositions shall be determined by referee methods specified by such as ISO *****(to be published).

NOTE

1 Reference material(RM) is a material one or more of whose element concentration are sufficiently homogeneous and assigned by referee methods(definitive method such as electrochemical, gravimetric and titrimetric method, and spectrometric method calibrated by pure metal or pure chemical compound).

2 Certified reference material(CRM) is a reference materials, accompanied by a certificate, one or more whose element concentration are certified by a procedure which establishes its traceability to an accurate realisation of the unit in which the property values are expressed and for which each certified value is accompanied by an uncertainty at a stated level of confidence.

6.3.3 Determination of the sputtering rate of calibration samples

The term *sputtering rate* is here understood to be equivalent to the mass loss rate during sputtering in the glow discharge. In order to determine this quantity for the calibration samples, the following procedure is recommended:

- If laboratory means are available, measure the density of each calibration sample. A suitable method for homogeneous samples is sample mass divided by sample volume where the sample volume is measured by immersion of the sample in water following the method of Archimedes. For regularly shaped samples, including coatings, the volume can be calculated from the dimensions of the sample. The accuracy of the measured density should be better than 5%.
- If the procedure of a) is not available, calculate a density,

$$\rho = 100 / \sum_i m_i / \rho_i$$

where m_i in the mass percent of element i in the sample;

ρ_i is the theoretical density of element i ;

Proceed with sputtering rate determinations as follows:

- prepare the sample surface according to recommendations from the instrument manufacturer;
- adjust the glow discharge current and voltage to those selected in 6.2;
- sputter the sample for a time estimated to result in a crater 20 •m to 40 •m deep, recording the total sputtering time;

- d) repeat c) several times if the sample surface area is sufficiently large, recording the total sputtering time for each crater;
- e) measure the average depth of each crater by means of an optical or mechanical profilometer device, performing at least 4 profile traces in different directions across the centre of the crater;
- f) calculate the sputtered volume of each crater, the sputtered mass as the volume multiplied by the density of the sample;
- g) calculate the sputtering rate for each crater as the mass loss divided by the total sputtering time;
- h) calculate the average sputtering rate and the standard deviation from the measurements of each crater.

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

NOTE

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

6.3.4 Emission intensity measurements of calibration samples

The procedure for measuring the calibration samples is as follows.

- a) Prepare the surfaces of the calibration samples according to the instrument manufacturers instructions.
- b) Adjust the instrument to the current and voltage settings selected in 6.2, a preburn time of 100 s to 200 s and a signal integration time of 5 s to 30 s.
- c) Measure the emission intensities of the analytes zinc, aluminium, nickel, iron, silicon, copper and lead for each calibration sample. Additional analytes, which are present in the calibration samples, may be measured simultaneously. The units in which the intensities are given is of no importance, commonly used units are counts per second (cps) or volts (V). Measure each sample at least two times and calculate the average values.

6.3.5 Calculation of calibration constants

Follow one of the procedures given in Annex A, that is appropriate for the instrument and software system available.

NOTE:

Depending on the type of source, mode of operation and the calibration samples chosen, the calibration graphs for some elements may show a large separation between samples from different matrices. The separation typically occurs between two matrix groups: one group including low alloy steel, stainless steel and brass, and a second group including aluminium and aluminium-zinc alloys. This separation has been noted particularly in calibration graphs for zinc, but is present in all other elemental calibration graphs where samples from both matrix groups are included. This separation is proof of a difference in emission yield, and has been shown to be well correlated to matrix-dependent variations in the glow discharge plasma impedance. Consequently, it is a considerably larger problem with RF sources operated in the constant applied power – constant pressure mode than e.g. DC sources operated in a constant current – variable pressure mode. The best way to minimise the effect is an active pressure regulation system which maintains constant plasma impedance during calibration and analysis. If this or some other facility is provided by the manufacturer to minimise this effect, it should be used. Otherwise the solution is to choose, from each calibration curve, calibration samples which most resemble the samples to be analysed. This normally does not present any special difficulty. For zinc, for example, when analysing aluminium-zinc coated steel, the brass samples are excluded from the calibration graph.

6.4 Verification of the analytical accuracy

- a) After establishing calibration graph, select a few coated or bulk reference materials independent from the set of calibration samples which contain the relevant analytes in concentrations as close as possible to those found in the coating types to be determined.
- b) Adjust the glow discharge operating parameters to those selected in 6.2, sputter the reference material and carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the coating completely and continue well into the base material.
- c) Convert the relationship between the emission intensities and time in second to the relationship between mass fraction percent of each analyte and depth in pm using the calibration graph established in 6.3.5 and the algorithm described in Annex A.2 and A.3, and plot them in chart.
- d) Calculate and/or read out thickness of coating, total sputtering depth and average chemical composition of each analyte from the chart (see A.4).
- e) Measure the average depth of the crater by means of an optical or mechanical profilometer device, performing at least 4 profile traces in different directions across the centre of the crater. Compare the total sputtering depth in the chart with the measured average depth of the crater by means of the profilometer. The difference should be within 5% (*unrealistic, 10% is suggested*).
- f) Calculate coating weight using the theoretical density of reference material, if necessary, and compare the result with the assigned values of the coating weight of the reference material. The difference should be within 5% (*unrealistic, 10% is suggested*).
- g) Check that the measured average chemical composition of each analyte is accurate to within the acceptable uncertainty relative to the assigned value of the reference materials. The acceptable uncertainty cannot be uniquely defined for all analytes, but for majors a relative accuracy better than 5% should be achievable in most cases.
- h) If the differences of three values, total sputtered depth, thickness of the coating (coating weight) and average chemical compositions, are within the tolerances described in f), g) and h) respectively, the calibration constants are acceptable.
- i) If any difference of the three is more than the specified tolerance, the calibration graph shall be re-established in accordance with 6.3.1 to 6.3.5 using other operating parameters of the glow discharge selected in 6.2 and/or reference materials.

NOTE: The coating weight of the reference material may be of insufficient accuracy. In such a case two of the three values, total sputtered depth and average chemical compositions may be evaluated in item h).

6.4.1 Verification and drift correction

It is not necessary to prepare a new calibration for each series of determinations of unknown samples. Instead, a only a limited number of the calibration samples are re-run in order to determine the instrumental drift in sensitivity and background for each spectral channel used in the method. For each channel, a high and a low intensity point is required. The measured intensities are then corrected for the drift prior to the calculation of the quantitative results. This procedure, referred to as *drift correction*, is routinely employed in both spark discharge optical emission and X-ray fluorescence spectrometry for bulk analysis.

In routine work, before determining test samples, verification and if necessary drift correction of the calibration shall be conducted in accordance with following procedure at least once a day.

- a) Select two CRMs or RMs of high and low concentration of chemical composition which are used in calibration.

- b) Adjust the glow discharge operating parameters to those selected in 6.2, sputter the sample until a time emission intensity becomes stable and calculate \bar{a} mean based on integration of the signal during 3 – 30 seconds. Convert the mean to chemical composition, expressed as %(m/m) using the present calibration constants.
- c) Compare the results with assigned value of CRMs and/or RMs and correct the drift of calibration graph so that determined value of each analyte coincides with the assigned value of CRMs and/or RMs within the specified tolerance.

6.5 Determination of a test sample

- a) Prepare a test sample in accordance with section 5.
- b) Adjust the glow discharge operating parameters to those selected in 6.2, sputter the test sample and carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the coating completely and continue well into the base material.
- c) Convert the emission intensity vs. time depth profile mass fraction percent of each analyte and depth in pm using the calibration established in 6.3 and the algorithms described in Annex A, and plot in a chart.
- d) Measure the average depth of the sputtered crater by means of an optical or mechanical profilometer device and compare with the total sputtered depth according to the chart.
- e) Measure each sample in at least two positions on one side.

In order to compare with results determined by chemical methods, measure five points and average.

7 Expression of the results

All analytical information obtained is contained in the quantitative depth profile (figure 1).

Galvanneal

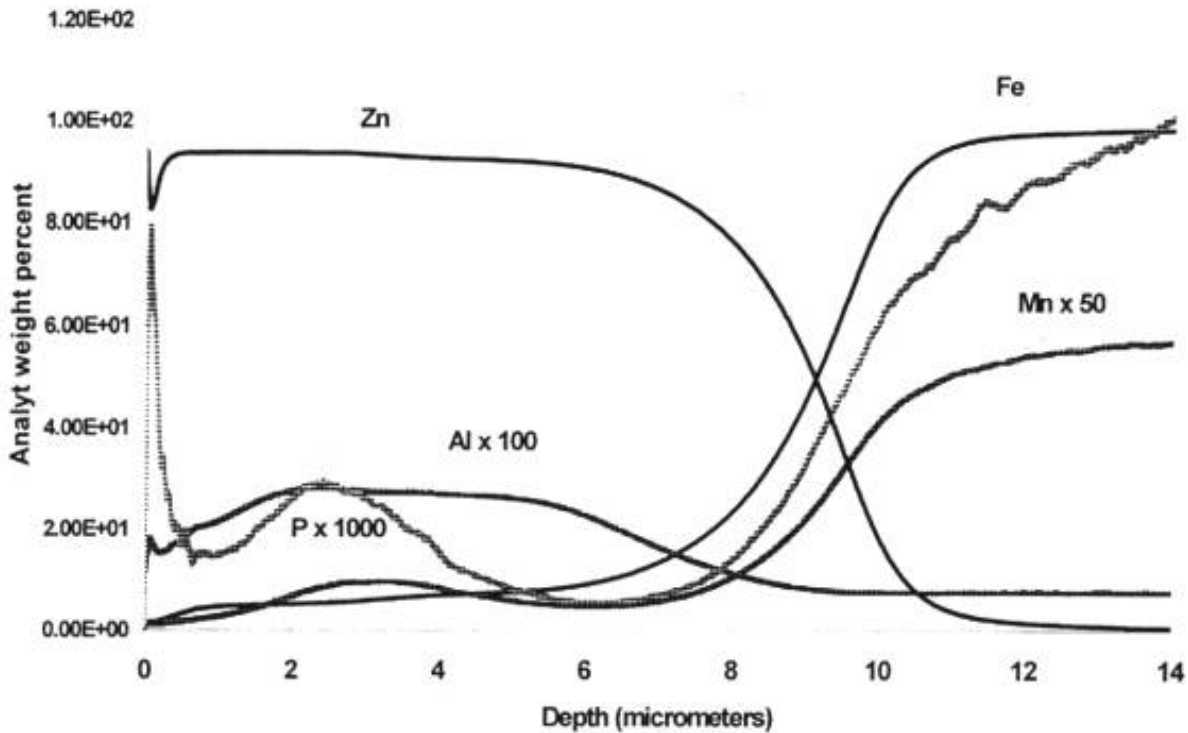


Figure 1 — Quantitative depth profile of a Galvanneal (ZnFe) coating on steel

7.1 Determination of total coating weight

In order to determine the total coating weights per element, the area under each curve is integrated for the total depth of the coating. The relevant algorithms are given in Appendix A.2. For the major elements, the following recommendation for determination of the integration depth is given.

- Determine the coating thickness as the depth where the concentration of the major element is reduced to 50% of the average value in the coating.
- Determine the width of the interface region (= the practical depth resolution) as the difference between the two points in depth where the concentrations of the major element are 84% and 16% respectively of the average value in the coating.
- Determine the integration depth as the sum of the coating thickness and the interface width.

7.2 Determination of average concentrations

The average concentrations of each element are determined as the fractions of the sum of the coating weights of all elements present in the coating.

8 Precision

To be investigated

9 Test report

The test report shall include the following information:

- a) all information necessary for the identification of the sample;
- b) the laboratory and the date of analysis;
- c) the method used, by reference to this International Standard;
- d) the analytical results and the form in which they are expressed;
- e) any unusual features noted during the determination;
- f) any operation not specified in this International Standard or any optional operation, which may have influence the results.

Annex A (Normative)

Calculation of calibration constants and quantitative evaluation of depth profiles

A.1 Calculation of calibration constants

In this standard, the emission yield $R_{i\lambda}$ of element i and spectral line λ is defined by the following equation:

$$R_{i\lambda} = \left[\frac{(I_{i\lambda} - B_{\lambda}) \cdot \Delta t}{m_i} \right] \quad (1)$$

where

- m_i is the sputtered mass of element i during time increment Δt
- $I_{i\lambda}$ is the emission intensity of spectral line λ of element i ;
- B_{λ} is the spectral background intensity at wavelength λ

As defined here, $R_{i\lambda}$ depends on atomic as well as instrument specific parameters. It is therefore necessary to determine the emission yields for each apparatus used.

The quantity m_i is also given by the equation:

$$m_i = q_s \cdot c_{is} \cdot \Delta t \quad (2)$$

where

- q_s is the sputtering rate of sample s ;
- c_{is} is the concentration of element i in sample s ;

It can be inferred from equation (1), that by plotting the sputtered mass of element i as a function of the time-integrated intensity of the corresponding spectral line, the inverse of the emission yield is obtained as the slope of the calibration curve.

Combining equation (1) and (2) gives the following alternative expression for determination of the emission yield:

$$q_s * c_{is} = \frac{(I_{i\lambda} - b_\lambda)}{R_{i\lambda}} \quad (3)$$

In practical analytical work, it is recommended to use equation (3) for the determination of the emission yields rather than equation (1). This equation can conveniently be modified to non-linear calibration curves by incorporating a second-order term:

$$q_s * c_{is} = \frac{I_{i\lambda}}{R_{i\lambda}} + k * \left(\frac{I_{i\lambda}}{R_{i\lambda}} \right)^2 - \frac{B_\lambda}{R_{i\lambda}}$$

(3b)

where

k is a constant describing the degree of non-linearity

If necessary also a third order term can be added to equation (3b). The actual calibration constants shall be obtained by regression analysis of the calibration data according to a least square fit algorithm.

A third form of calibration function based on the concept of constant emission yield, is obtained by multiplying the measured emission intensities of each calibration standard with a sputtering rate correction factor, which normalises the intensities to that of a reference material of well determined sputtering rate. This procedure, commonly referred to as the intensity normalisation technique, gives the following expression for calibrating with respect to sample concentrations:

$$c_{is} = k_{i\lambda} * c_{is} = k_{i\lambda} * I_{i\lambda} * \left(\frac{q_{ref}}{q_s} \right) - B_{\lambda c} \quad (4)$$

where

$k_{i\lambda}$ is equal to $1/(R_{i\lambda} * q_{ref})$

q_{ref} is the sputtering rate of the selected reference material;

q_{ref} is the sputtering rate correction factor;

$B_{\lambda c}$ is the spectral background at wavelength λ , given in concentration units (often referred to as background equivalent concentration) .

The main reason why equation (4) is often used for calibration in commercially available systems is that it has the same general form as the calibration functions conventionally used in bulk analysis, where the actual concentration is plotted as a function of emission intensity. The number "q", is normally selected as the sputtering rate of some frequently used base material for calibration standards, e.g. pure iron. This has the effect that for several iron based calibration samples, the sputtering rate correction factor is close to unity, If q_{ref} is set equal to 1 (unity sputtering rate), equation (4) becomes numerically equivalent to equation (3).

NOTE 1 The emission yields vary with the current, voltage and possibly the pressure (4) . It is therefore essential that these parameters are kept as closely as possible at the same levels during measurement of coated samples as during calibration. Since it is impossible in practice to maintain all three parameters constant for all samples, priority is given to maintaining current and voltage constant, utilising the pressure as a variable parameter. There exists a method to correct for voltage and current variations by means of an empirically derived function (4) and this type of correction is often implemented in software based on the intensity normalisation method according to equation (4). However, such corrections for voltage and current are not to be included in this standard method. If available in the spectrometer software, the user shall therefore ensure that the voltage to current corrections are disabled in order to implement the method correctly.

NOTE 2 The spectral background terms in equation (1), (3) and (4) are not true constants, they are more or less matrix dependent as was pointed out in section 4.1.2. In practical work, it is advisable to always select the lowest measured intensity as fixed the background for each spectral line.

NOTE 3 All commercially available instruments manufactured today have provisions to subtract additional background signals from other analyte elements (line interference corrections). Where applicable, such corrections should be implemented.

A.2 Calculation of concentrations and sputtered mass

The calculation of elemental concentrations and sputtered mass can proceed according to two different sets of algorithms described below, depending on which calibration function that was used according to section 6.3.4. The final results are, however, equivalent.

A.2.1 Calculation based on calibration for sputtered mass per element

If equation (1) or (3) was used for calibration, the following calculation steps are to be carried out.

For each segment j and corresponding time increment Δt_i of the depth profile, calculate the sputtered mass m_{ij} of element i according to the equation:

$$m_{ij} = \left[(I_{it\lambda} - B_\lambda) \cdot \frac{\Delta t}{R_{i\lambda}} \right] \quad (5)$$

If equation (3b) has been used, the second order term is added in a straight-forward manner.

Provided that the sum of all determined elements constitute $> 98\%$ of the analysed material, calculate the total sputtered mass, M_j of segment j of the depth profile using the equation:

$$M_j = \sum M_{ij} \quad (6)$$

The concentration c_{ij} of element i in segment j is given by the equation:

$$c_{ij} = 100 \cdot \frac{m_{ij}}{M_j} \quad (7)$$

where c_{ij} is given in units of % by mass.

The total sputtered mass, M_i of element i in any arbitrary section of the depth profile is given by the equation

$$M_i = \sum_j M_{ij} \quad (8)$$

The analyst determines where the summation range over segments j .

A.2.2 Calculation based on calibration for concentrations of the elements

If equation (4) was used for calibration, the following calculation steps are to be carried out.

Provided that the sum of all determined elements constitute > 98% of the analysed material, the concentration c_{ij} of element i in segment j is given by the equation:

$$c_{ij} = \frac{(k_{i\lambda} * I_{ij\lambda} - B_{\lambda c})}{\sum_i (k_{i\lambda} * I_{ij\lambda} - B_{\lambda c})} \quad (9)$$

where

$k_{i\lambda}$, B_{λ} are the calibration constants calculated from equation (4).

NOTE Equation (9) incorporates a sum normalisation of all concentrations to 100 %.

For each segment, j , of the depth profile, calculate the sputtering rate, q_j using the equation:

$$q_j = q_{ref} * \sum_i \frac{(K_{i\lambda} * I_{ij\lambda} - B_{\lambda c})}{100} \quad (10)$$

where

q_{ref} is the sputtering rate of the selected reference material.

For each segment, j , and corresponding time increment, Δt_i , of the depth profile, the sputtered mass, m_{ij} of the element is given by the equation:

$$m_{ij} = q_i * c_{ij} * \Delta t_i \quad (11)$$

The total sputtered mass, M_i of element i is calculated according to equation (8) of section 7.1.1,

A.3 Calculation of sputtered depth

A.3.1 General

The analytical method described in this standard determines the sputtered mass and concentrations of each element. In order to determine the sputtered depth, it is necessary to calculate also the volume of the sputtered material. In order to do so, the *density* of the sputtered material shall be known. This can be estimated from the elemental composition and the densities of the pure elements.

There are two existing methods to calculate the sputtered depth, both of which can be utilised for the purposes of this standard method.

A.3.2 Calculation based on fractional volumes

For each segment, j , of the depth profile, calculate the sputtered volume, V_j , using the equation:

$$V_i = \sum_i \frac{m_{ij}}{\rho_i} \quad (11)$$

where

ρ_i is the density of element i.

For each segment, j, of the depth profile, calculate the depth, D_j , of that segment relative to the sample surface using the equation:

$$D_j = \sum_i \frac{V_j}{A_s} \quad (12)$$

where

A_s , is the area of the sputtered spot.

A.3.3 Calculation based on averaged density

For each segment, j, of the depth profile, calculate the atomic fraction, a", using the equation:

$$a_{ij} = \frac{\left(\frac{c_{ij}}{w_i} \right)}{\sum_i \frac{c_{ij}}{w_i}} \quad (13)$$

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:

$$\rho_j = \sum_i a_{ij} * \rho_i$$

For each segment, j, of the depth profile, calculate the sputtered volume, V_j using to the equation:

Annex 8 (informative)

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