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

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

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## Foreword

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

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

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

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

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

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

## 1 Scope

This International Standard specifies a glow discharge optical emission spectrometric method for the determination of the thickness, mass per unit area and chemical composition of metallic surface coatings consisting of zinc- and/or aluminium-based materials. The alloying elements considered are nickel, iron, silicon, lead and antimony.

This method is applicable to

zinc contents between 0,01 mass % and 100 mass %;

aluminium contents between 0,01 mass % and 100 mass %;

nickel contents between 0,01 mass % and 20 mass %;

iron contents between 0,01 mass % and 20 mass %;

silicon contents between 0,01 mass % and 10 mass %;

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

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

## 2 Normative references

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

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

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

ISO 17925, *Zinc and/or aluminium based coatings on steel — Determination of coating mass per unit area and chemical composition — Gravimetry, inductively coupled plasma atomic emission spectrometry and flame atomic absorption spectrometry*

## 3 Principle

The analytical method described here involves the following processes:

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

- b) Excitation of the analyte atoms in the plasma formed in the glow discharge device.
- c) Spectrometric measurement of the intensities of characteristic emission spectral lines of the analyte atoms as a function of sputtering time (depth profile).
- d) Conversion of the depth profile in units of intensity versus time to mass fraction versus depth by means of calibration functions (quantification). Calibration of the system is achieved by measurements on calibration samples of known chemical composition and measured sputtering rate.

## 4 Apparatus

### 4.1 Glow discharge optical emission spectrometer

Required instrumentation includes an optical emission spectrometer system consisting of a Grimm type<sup>[1]</sup> or similar glow discharge source (direct current or radio frequency powered) and a simultaneous optical spectrometer as described in ISO 14707, incorporating suitable spectral lines for the analyte elements (see Annex B for suggested lines).

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

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

### 4.2 Minimum performance requirements

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#### 4.2.1 General

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

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

#### 4.2.2 Minimum repeatability

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

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

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

### 4.2.3 Detection limit

#### 4.2.3.1 General

Detection limits are instrument-dependent and matrix-dependent. Consequently, the detection limit for a given analyte cannot be uniquely determined for every available instrument or for the full range of Zn/Al-based alloys considered here. For the purposes of this International Standard, the detection limit for each analyte will be acceptable if it is equal to or less than one-fifth of the lowest mass fraction expected in the coating or one-fifth of the lower end of the range of mass fractions quoted in Clause 1 of this International Standard, whichever is greater.

#### 4.2.3.2 SNR method

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

- 1) Select a bulk sample to be used as a blank. The composition of the sample shall be similar to that of the coatings to be analysed in terms of the elemental composition of the matrix. Further, it shall be known to contain less than 0,1 µg/g of the analyte.
- 2) Perform ten replicate burns on the blank. For each burn, acquire the emission intensity at the analytical wavelength for 10 s. These are the background emission intensity measurements. The glow discharge conditions used shall be the same as those that will be used in the analysis of the coated samples. For each measurement, the blank shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the emission intensity. Use an unspattered area of the surface of the blank for each individual burn.
- 3) Compute the detection limit, expressed as a mass fraction, using the following equation:

$$DL = \frac{3 \times S}{m} \quad \text{ISO 16962:2005} \quad (1)$$

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where

DL is the detection limit;

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

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

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

#### 4.2.3.3 SBR-RSDB method

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

- 1) Select a bulk sample that has a matrix composition that is similar to that of the coatings to be analysed, and for which the mass fraction of the analyte is greater than 0,1 % and known. If an analytical transition that is prone to self-absorption (see 6.1) is to be used, then the mass fraction of the analyte shall not exceed 1 %.
- 2) Perform three replicate burns on the chosen sample. For each burn, integrate the emission intensity at the analytical wavelength for 10 s. The glow discharge conditions used shall be similar to those that will be used in the analysis of the coated samples. For each measurement, the sample shall be preburned at these conditions for a sufficient length of time to achieve stable signals prior to the quantification of the

emission intensity. Use an unsputtered area of the surface of the sample for each individual burn. Average the three replicate emission intensities.

- 3) Select a peak-free region of the emission spectrum within 0,2 nm of the analytical peak. Perform ten replicate burns on the chosen sample. For each burn, integrate the intensity at the peak-free region for 10 s. These are the measurements of the background intensity. The glow discharge conditions and preburn shall be the same as those used in step 2. Once again, use an unsputtered area of the surface of the sample for each individual burn. Compute the average and relative standard deviation of the 10 replicate measurements.
- 4) Calculate the detection limit using the following equation:

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

where

DL is the detection limit;

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

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

B is the average background intensity from step 3;

S is the average peak intensity from step 2.

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

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## 5 Sampling

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

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

## 6 Procedure

### 6.1 Selection of spectral lines

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



elements. In Annex B, some suggestions concerning suitable spectral lines are given. Spectral lines other than those listed may be used, so long as they have favourable characteristics.

## 6.2 Optimizing the glow discharge spectrometer system settings

### 6.2.1 General

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

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

There are often tradeoffs among the three specified aims.

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

### 6.2.2 Setting the discharge parameters of a dc source

#### 6.2.2.1 General

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

#### 6.2.2.2 Constant applied current and voltage

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

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

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

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

#### 6.2.2.3 Constant applied current and pressure

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

somewhere in the middle of the recommended range is used. Sputter a typical coated test sample, and adjust the pressure until a voltage of approximately 600 V is attained in the coating.

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

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

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

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

### 6.2.3 Setting the discharge parameters of an rf source

#### 6.2.3.1 General

Currently, most rf sources are operated with constant applied power and constant pressure. Other modes also exist, such as constant applied voltage and pressure, and constant effective power and applied voltage. These modes are likely to become more common in the future. All rf operational modes are allowed in this International Standard provided they meet the three aims listed in 6.2.15. In the following, separate instructions are provided on how to set the parameters for the operational modes that are currently used regularly.

#### 6.2.3.2 Constant applied power and pressure

The two control parameters are applied power and pressure. First set the applied power and adjust the source pressure to those suggested by the manufacturer. If recommended values are not available, set the applied power and pressure to somewhere in the middle of the ranges commonly used for depth profiling of metal samples. Measure the penetration rate (i.e. depth per unit time) on an iron or steel sample. Adjust the power to give a penetration rate of about 2  $\mu\text{m}/\text{min}$  to 3  $\mu\text{m}/\text{min}$ .

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

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

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

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

#### 6.2.3.3 Constant applied power and dc bias voltage

The two control parameters are applied power and dc bias voltage. First set the applied power and adjust the source pressure to attain a dc bias typical of those suggested by the manufacturer. If recommended values

are not available, set the applied power and dc bias voltage to somewhere in the middle of the ranges commonly used for depth profiling of metal samples. On instruments equipped with active pressure control, this can be achieved automatically. Measure the penetration rate (i.e. depth per unit time) on an iron or steel sample. Adjust the power to give a penetration rate of about 2  $\mu\text{m}/\text{min}$  to 3  $\mu\text{m}/\text{min}$ .

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

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

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

Re-measure the penetration rate on the iron or steel sample and adjust the applied power if necessary to return to about 2  $\mu\text{m}/\text{min}$  to 3  $\mu\text{m}/\text{min}$ . Repeat the cycles of power and dc bias voltage adjustment until no significant change is noted in the penetration rate or crater shape. If this is not the case, readjust the dc bias voltage until the correct value is attained. Note the power and dc bias voltage used in units provided by the instrument. These conditions are then used during calibration and analysis.

#### 6.2.3.4 Constant effective power and rf voltage

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

Set the power supply for the glow discharge source to constant effective power/constant rf voltage operation. First set the power to typical values recommended by the manufacturer. If no recommended values are available, set the rf voltage to 700 V and the power to a value in the range 10 W to 15 W for a 4 mm anode, for example. If no previous knowledge about the optimum power is available, it is recommended that, to start with, a value somewhere in the middle of the recommended range is used.

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

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

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

Re-measure the penetration rate on the iron or steel sample and adjust the applied power if necessary to return to about 2  $\mu\text{m}/\text{min}$  to 3  $\mu\text{m}/\text{min}$ . Repeat the cycles of power and dc bias voltage adjustment until no significant change is noted in the penetration rate or crater shape. If this is not the case, readjust the dc bias voltage until the correct value is attained. Note the power and dc bias voltage used, in units provided by the instrument. These conditions are then used during calibration and analysis.

#### 6.2.4 Setting the high voltage of the detectors

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

#### 6.2.5 Adjusting the discharge parameters

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

repeat this procedure for a number of control parameter combinations until stable emission conditions are obtained.

### 6.2.6 Optimizing crater shape

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

### 6.2.7 Preliminary performance test

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

## 6.3 Calibration

### 6.3.1 General

Calibration of the system consists of determining, for each analyte and spectral line, the analytical response curve as described in either Clause A.2 or Clause A.3 in Annex A. In order to carry out the calibration, it is necessary to know both the chemical composition and the sputtering rates (mass loss rates) of the calibration samples.

### 6.3.2 Calibration samples

#### 6.3.2.1 General

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

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

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

#### 6.3.2.2 Brass calibration samples

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

#### 6.3.2.3 Zn-Al alloy samples

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