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

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Foreword

This translation has been made based on the original Japanese Industrial Standard established by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee according to the proposal for establishment of Japanese Industrial Standard submitted by Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law.

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

Introduction

This Japanese Industrial Standard has been prepared based on the first edition of **ISO 16962** published in 2005 without modifying the technical contents.

The portions underlined with dots are the matters not given in the corresponding International Standard.

1 Scope

This 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 %.

NOTE : The International Standard corresponding to this Standard is as follows.

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

In addition, symbols which denote the degree of correspondence in the contents between the relevant International Standard and **JIS** are IDT (identical), MOD (modified), and NEQ (not equivalent) according to **ISO/IEC Guide 21**.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

JIS G 0417 *Steel and iron—Sampling and preparation of samples for the determination of chemical composition*

NOTE : Corresponding International Standard: ISO 14284 *Steel and iron—Sampling and preparation of samples for the determination of chemical composition* (IDT)

JIS K 0144 *Surface chemical analysis—Glow discharge optical emission spectrometry (GD-OES)—Introduction to use*

NOTE : Corresponding International Standard: ISO 14707 *Surface chemical analysis—Glow discharge optical emission spectrometry (GD-OES)—Introduction to use* (IDT)

JIS Z 8402-1 *Accuracy (trueness and precision) of measurement methods and results—Part 1: General principles and definitions*

NOTE : Corresponding International Standard: ISO 5725-1 *Accuracy (trueness and precision) of measurement methods and results—Part 1: General principles and definitions* (IDT)

JIS Z 8402-2 *Accuracy (trueness and precision) of measurement methods and results—Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

NOTE : Corresponding International Standard: ISO 5725-2 *Accuracy (trueness and precision) of measurement methods and results—Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method* (IDT)

JIS Z 8402-6 *Accuracy (trueness and precision) of measurement methods and results—Part 6: Use in practice of accuracy values*

NOTE : Corresponding International Standard: ISO 5725-6 *Accuracy (trueness and precision) of measurement methods and results—Part 6: Use in practice of accuracy values* (IDT)

ISO 17925:2004 *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 [1] or similar glow discharge source (direct current or radio frequency powered) and a simultaneous optical spectrometer as described in **JIS K 0144**, 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 Standard a speed of 2 measurements/second per spectral channel may be acceptable.

4.2 Minimum performance requirements

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 Standard, the detection limit for each analyte shall be obtained as specified in 4.2.3.2 or 4.2.3.3 and it 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 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:

$$DL = \frac{3 \times s}{m} \dots\dots\dots (1)$$

where, DL : the detection limit;

s : the standard deviation of the ten background intensity measurements performed in step 2);

m : the analytical sensitivity¹⁾ derived from the instrument calibration.

Note ¹⁾ 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:

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

where, DL : the detection limit;

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

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

B : the average background intensity from step 3);

S : 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.

5 Sampling

As appropriate, carry out sampling in accordance with **JIS G 0417** 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.

NOTE : Acetone should be guaranteed type equivalent specified in **JIS K 8034** and ethanol should be guaranteed type equivalent specified in **JIS K 8101**.

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 **JIS K 0144**.

NOTE : "Accuracy (trueness and precision)" used in this Standard shall be in accordance with **JIS Z 8402-1**.

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 regulation²⁾]. 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.

Note ²⁾ The method to regulate gas pressure in order to keep current constant.

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, re-adjust 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 Standard provided they meet the three aims listed in **6.2.1**. 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.