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

Analyse chimique des surfaces — Analyse de films d'oxyde de métal par spectrométrie d'émission optique à décharge luminescente

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

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

This second edition cancels and replaces the first edition (ISO/TS 25138:2010), which has been technically revised. The main changes compared to the previous edition are as follows:

- the element Zr has been added to the Scope;
- the description of the apparatus has been modified to include spectrometers with solid-state array detectors of the types CCD and CID;
- Clause 6 has been modified for more clarity, and to include the spectrometer types;
- Clause 8 has been modified for more clarity, particularly in the recommendations for calibration samples.

A list of all parts in the ISO TS 25138 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

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

1 Scope

This document describes a glow-discharge optical-emission spectrometric method for the determination of the thickness, mass per unit area and chemical composition of metal oxide films.

This method is applicable to oxide films 1 nm to 10 000 nm thick on metals. The metallic elements of the oxide can include one or more from Fe, Cr, Ni, Cu, Ti, Si, Mo, Zn, Mg, Mn, Zr and Al. Other elements that can be determined by the method are O, C, N, H, P and S.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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

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

ISO 16962:2017, *Surface chemical analysis — Analysis of zinc- and/or aluminium-based metallic coatings by glow-discharge optical-emission spectrometry*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
verification
confirmation, through the provision of objective evidence, that specified requirements have been fulfilled

[SOURCE: ISO 9000:2015, 3.8.12]

3.2
validation
confirmation, through the provision of objective evidence, that the particular requirements for a specific intended use or application have been fulfilled

[SOURCE: ISO 9000:2015, 3.8.13]

4 Principle

The analytical method described here involves the following processes.

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

b) Excitation of the analyte atoms in the plasma formed in the glow-discharge device.

c) Spectrometric measurement of the intensities of characteristic spectral-emission lines of the analyte atoms as a function of sputtering time (qualitative depth profiling).

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.

e) Preparation of the sample to be analysed, generally in the form of a flat plate or disc of dimensions appropriate to the instrument or analytical requirement (round or rectangular samples with a width of more than 5 mm, generally 20 mm to 100 mm, are suitable).

5 Apparatus

5.1 Glow-discharge optical-emission spectrometer

5.1.1 General

The required instrumentation includes an optical-emission spectrometer system consisting of a Grimm type[1] or similar glow-discharge source (direct-current or radio-frequency powered) and a simultaneous optical spectrometer as described in ISO 14707, capable of providing suitable spectral lines for the analyte elements. It is also common to combine this with a sequential spectrometer (monochromator), allowing the addition of an extra spectral channel to a depth profile measurement. An array-type detector, such as a charge coupled device (CCD) or a charge injection device (CID) can also be used for simultaneous detection to cover a wide spectral range of the analytical 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 principle of determination is based on continuous sputtering of the surface metal oxide, the spectrometer shall be equipped with a digital readout system for time-resolved measurement of the emission intensities. A system capable of a data acquisition speed of at least 300 measurements/second per spectral channel is recommended, but, for a large number of applications, speeds of >50 measurements/second per spectral channel are acceptable.

5.1.2 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 samples. For applications where several 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 should therefore be avoided for the determination of major elements. Suggestions concerning suitable spectral lines are given in Annex B. Spectral lines other than those listed may be used, so long as they have favourable characteristics.

5.1.3 Selection of glow-discharge source type

5.1.3.1 Anode size

Most GD-OES instruments on the market are delivered with options to use various anode diameters, 2 mm, 4 mm and 8 mm being the most common. Some older instruments have one anode only, usually 8 mm, while the most commonly used anode in modern instruments is 4 mm. A larger anode requires larger samples and higher power during analysis; therefore the sample 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 metal oxide. 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 samples due to e.g. surface layers of poor heat conductivity and/or very thin samples. In such cases, the smaller 2 mm anode is preferable, even if there is some loss of analytical sensitivity.

5.1.3.2 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 samples; hence this is the only type that can be used for e.g. polymer coatings and insulating oxide layers. On the other hand, it is technically simpler to measure and control the electrical source parameters (voltage, current, power) of a DC type. Several commercially available GD-OES systems can be delivered with the option to switch between DC and RF operation, but RF-only systems are becoming increasingly common. In short, there are a very large number of applications where DC or RF sources can be used and several where only an RF source can be used.

5.1.3.3 Mode of operation

Both DC and RF sources can be operated in several different modes with respect to the control of the electrical parameters (current, voltage, power) and the pressure. There are several reasons for this:

- "historical" reasons (older instruments have simpler but functional power supplies, while the technology has evolved so newer models have more precise and easier-to-operate source control);
- different manufacturers have chosen different solutions for source control;
- there are some application-related issues where a particular mode of operation is to be preferred.

This document gives instructions for optimizing the source parameters based on several available modes of operation. The most important reason for this is to make these instructions comprehensive so as to include several types of instrument. In most applications, there is no major difference between these modes in terms of analytical performance, but there are other differences in terms of practicality and ease of operation. For instance, a system equipped with active pressure regulation will automatically be adjusted to the same electrical source parameters every time a particular analytical method is used. Without this technology, some manual adjustment of the pressure to achieve the desired electrical source parameters is normally required.

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

6 Adjusting the glow-discharge spectrometer system settings

6.1 General

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

For an optical system with photomultiplier detectors in fixed spectral positions, 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. For an optical system with CCD detectors, the corresponding control is to check that the wavelength calibration is correct, following the procedure given by the instrument manufacturer.

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 sample, to reduce the analysis time without overheating the sample;

b) good crater shape, for good depth resolution;

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

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

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

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.

NOTE 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.

6.2 Setting the parameters of a DC source

6.2.1 Constant applied current and voltage

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 (current set by the power supply, voltage adjusted by pressure/gas flow regulation). Then set the current and voltage to the typical values recommended by the manufacturer. Alternatively, set the power supply to constant voltage/constant current operation (voltage set by the power supply, current adjusted by pressure/gas flow regulation). If no recommended values are available, set the voltage to 700 V and the current to a value in the range 5 mA to 10 mA for a 2 mm or 2,5 mm anode, 15 mA to 30 mA for a 4 mm anode or 40 mA to 100 mA for a 7 mm or 8 mm anode. If no previous knowledge of the optimum current is available, it is recommended to start with a value somewhere in the middle of the recommended range.

NOTE For the purposes of this document, there is no difference between the two alternative modes of operation described above.

6.2.1.1 Setting the high voltage of the detectors

Select test samples with surface layers of all types to be determined. For all test samples, run the source while observing the output signals from the detectors for the analyte atoms. Adjust the high voltage of the photomultiplier (PMT) 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. For array type detectors (CCD and CID), adjust the integration time in the same way as the high voltage for PMT.

6.2.1.2 Adjusting the source 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 metal oxide completely and continue well into the base material. By observing the emission intensities as a function of sputtering time (often referred to as the qualitative depth profile), verify that the selected source settings give stable emission signals throughout the depth profile and into the substrate. If this is found not to be the case, reduce one of the control parameters by a small amount and sputter through the metal oxide again. If the stability is still unsatisfactory, reduce the other control parameter by a small amount and repeat the measurements. If found necessary, repeat this procedure for a number of control parameter combinations until stable emission conditions are obtained.

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

6.2.1.3 Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a sample with a metal oxide typical of the test samples to be analysed to a depth of about 10 µm to 20 µm, but still inside the metal oxide. This is only possible for applications where surface metal oxide layers of such thickness are available. If no such sample is available, use a steel or brass sample. 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 6.2.1.3 is not compromised. In some cases, there is a certain trade-off between these two requirements.

6.2.2 Constant applied current and pressure

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

Set the high voltage of the detectors as described in 6.2.1.1.

Adjust the discharge parameters as described in 6.2.1.2, adjusting first the current and, if necessary, the pressure.

Optimize the crater shape as described in 6.2.1.3 by adjusting the pressure. These conditions are then used during calibration and analysis.

NOTE Before sputtering a new sample 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.

6.2.3 Constant voltage and pressure

The two control parameters are the 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 of approximately is attained 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, 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 6.2.1.1.

Adjust the source parameters as described in 6.2.1.2, adjusting first the voltage and if necessary the pressure.

Optimise the crater shape as described in 6.2.1.3, by adjusting the pressure. These conditions are then used during calibration and analysis.

NOTE 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.

6.3 Setting the discharge parameters of an RF source

6.3.1 General

The most common operating modes of RF sources are the following: constant applied power and constant pressure; constant applied voltage and constant pressure; or constant effective power and applied RF voltage (the RF voltage is defined here as the RMS voltage at the coupling electrode without DC bias). In addition, the mode constant applied power and DC bias voltage is sometimes used, but less common. All RF operational modes are allowed in this document, provided they meet the three aims listed in 6.1. In the following, separate instructions are provided on how to set the parameters for the different operational modes.

NOTE 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 W to 100 W, but it must be noted that the RF power losses in connectors, cables etc. vary considerably between different instrument models and the point of contact of the RF power to the sample. Typical power losses are in the range 10 % to 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.

6.3.2 Constant applied voltage and pressure

The two control parameters are the applied power and the pressure. First set the applied power and adjust the source pressure to the values suggested by the manufacturer. If recommended values are not available, set the applied power and pressure to somewhere in the middle of the ranges commonly used for depth profiling of metal samples. Measure the penetration rate (i.e. depth per unit time) on an iron or steel sample, 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 6.2.1.1.

Adjust the discharge parameters as described in 6.2.1.2, adjusting first the applied power and, if necessary, the pressure.

Optimize the crater shape as described in 6.2.1.3 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 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.