

# Teknisk specifikation

## SIS-ISO/TS 25138:2019

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### **Ytkemisk analys - Analys av metalloxidskikt med GD-OES**

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

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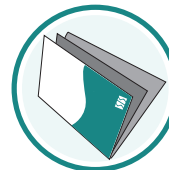
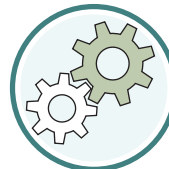
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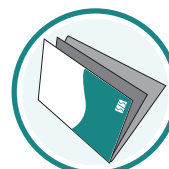
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Detta dokument ersätter SIS-ISO/TS 25138:2011, utgåva 1.

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This document supersedes SIS-ISO/TS 25138:2011, edition 1.

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Dokumentet är framtaget av kommittén för Kemiska analysmetoder för metaller, SIS/TK 122.

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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.

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](http://www.iso.org/directives)).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

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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](http://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](http://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]

## SIS-ISO/TS 25138:2019 (E)

### 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<sup>[1]</sup> 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<sup>[2][3]</sup> 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<sup>[8]</sup>. 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<sup>[8]</sup>, and this type of correction is implemented in the software of commercially available GD-OES systems.