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Surface chemical analysis — General procedures for quantitative compositional depth profiling by glow discharge optical emission spectrometry

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

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Surface chemical analysis — General procedures for quantitative compositional depth profiling by glow discharge optical emission spectrometry

Analyse chimique des surfaces — Modes opératoires généraux pour le profilage en profondeur compositionnel quantitatif par spectrométrie d'émission optique à décharge luminescente

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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.

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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 11505 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

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INTERNATIONAL STANDARD ISO 11505:2012(E)

Surface chemical analysis — General procedures for quantitative compositional depth profiling by glow discharge optical emission spectrometry

1 Scope

This International Standard describes a glow discharge optical emission spectrometric (GD-OES) method for the determination of the thickness, mass per unit area and chemical composition of surface layer films.

It is limited to a description of general procedures of quantification of GD-OES and is not applicable directly for the quantification of individual materials having various thicknesses and elements to be determined.

NOTE Any individual standard for a test material will have to specify a scope of a thickness of the surface layer as well as analyte elements, and include results of interlaboratory tests for validation of the methods.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

3 Principle

The analytical method described here involves the following processes:

a) cathodic sputtering of the surface layer in a direct current or radio frequency glow discharge device;

b) excitation of the analyte atoms and ions in the plasma formed in the glow discharge device;

c) spectrometric measurement of the intensities of characteristic spectral emission lines of the analyte atoms and ions as a function of sputtering time (qualitative depth profile);

d) conversion of the qualitative 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 specimens of known chemical composition and measured sputtering rate.

4 Apparatus

4.1 Glow discharge optical emission spectrometer

4.1.1 General

The required instrumentation includes an optical emission spectrometer system consisting of a Grimm type[10] 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

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lines for the analyte elements. Sequential optical spectrometers (monochromators) are not suitable, since several analytical wavelengths must be measured simultaneously at high data acquisition speed.

The inner diameter of the hollow anode of the glow discharge source should be in the range 1 mm to 8 mm. A cooling device for thin specimens, 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 layer, 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 a large number of applications, speeds of > 50 measurements/second per spectral channel are acceptable.

4.1.2 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 specimens. For applications where several of the analytes of interest are major elements in the specimens, special attention shall be paid to the occurrence of self-absorption of certain highly sensitive spectral lines (so-called resonance lines). Self-absorption causes nonlinear 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, as long as they have favourable characteristics.

4.1.3 Selection of glow discharge source type

4.1.3.1 Anode size

Most GD-OES instruments on the market are delivered with options to use various anode diameters, with 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 specimens and higher power during analysis; therefore the specimen 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 layer. 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 specimens due to, e.g. surface layers of poor heat conductivity and/or very thin specimens. In such cases, the smaller 2 mm anode is preferable, even if there is some loss of analytical sensitivity.

4.1.3.2 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 specimens; 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 also exist. 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.

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4.1.3.3 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 that 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 International Standard 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[11][12] forms the basis for calibration and quantification as described in this International Standard. The emission yield has been found to vary with the current, the voltage and, to a lesser extent, the pressure[17]. It is impossible in practice to maintain all three parameters constant for all test specimens, 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[17], and this type of correction is implemented in the software of commercially available GD-OES systems.

5 Adjusting the glow discharge spectrometer system settings

5.1 General

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

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 10–100 W, but it must be noted that the RF power losses in connectors, cables, etc. vary considerably between different instrument models. Typical power losses are in the range 10–50 % 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.

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.

For the optical system, 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.

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

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 5.2 and 5.3.

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.

5.2 Setting the discharge parameters of a DC source

5.2.1 Constant applied current and voltage

5.2.1.1 General

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. Then set the current and voltage to the 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 of 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.

5.2.1.2 Setting the high voltage of the detectors

Select test specimens with surface layers of all types to be determined. For all test specimens, 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 is ensured at the lowest analyte mass fraction without saturation of the detector system at the highest analyte mass fraction.

5.2.1.3 Adjusting the discharge parameters

For each type of test specimen, carry out a full depth profile measurement, sputtering it in the glow discharge for a sufficiently long time to remove the surface layers 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 surface layers 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 specimen surface layers; specimen cooling is beneficial in this regard.

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5.2.1.4 Optimizing the crater shape

If a suitable profilometer device is available, adopt the following procedure. Sputter a specimen with a surface layer typical of the test specimens to be analysed to a depth of about 10 µm to 20 µm, but still inside the surface layer. This is only possible for applications where surface layers of such thickness are available. If no such specimen is available, use a steel or brass specimen. 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 5.1.1.3 is not compromised. In some cases, there is a certain trade-off between these two requirements.

5.2.2 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 of 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 specimen, and adjust the pressure until a voltage of approximately 700 V is attained in the surface layer.

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the current and, if necessary, the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the control parameters. These conditions are then used during calibration and analysis.

Before sputtering a new specimen 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.

5.2.2.1 Constant applied voltage and pressure

The two control parameters are 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 is attained in the range of 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 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the voltage and if necessary the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the control parameters. These conditions are then used during calibration and analysis.

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.

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5.3 Setting the discharge parameters of an RF source

5.3.1 Constant applied power and pressure

The two control parameters are the applied power and the pressure. First set the applied power (forward 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 available for the instrument used. Measure the penetration rate (i.e. depth per unit time) on an iron or steel specimen, 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 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the applied power and, if necessary, the pressure.

Optimize the crater shape as described in 5.2.1.4 by adjusting the control parameters.

Remeasure the penetration rate on the iron or steel specimen 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.

5.3.2 Constant applied power and DC bias voltage

The two control parameters are the applied power and the DC bias voltage. First set the applied power and adjust the source pressure to attain a DC bias typical of the values 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 range commonly used for depth profiling of metal specimens. 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 specimen, adjusting the power to give a penetration rate of about 2 µm/min to 3 µm/min. Note that this procedure is only applicable to conducting surface layers, since the DC bias voltage cannot be measured for a specimen with a non-conducting surface layer.

Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the applied power and, if necessary, the DC bias voltage.

Optimize the crater shape as described in 5.2.1.4 by adjusting the control parameters.

Remeasure the penetration rate on the iron or steel specimen and adjust the applied power, if necessary, to return to about 2 µm/min to 3 µm/min. Repeat the cycle of power and DC bias voltage adjustment until no significant change is noted in the penetration rate or in the 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 for the instrument. These conditions are then used during calibration and analysis.

5.3.3 Constant effective power and RF voltage

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

Set the power supply for the glow discharge source to constant effective power/constant RF voltage operation. First set the power to a typical value 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 of 10 W to 15 W for a 4 mm anode, 5 W to 10 W for a 2 mm anode, to give an example. If no previous knowledge of the optimum power is available, it is recommended to start with a value somewhere in the middle of the recommended range.

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Set the high voltage of the detectors as described in 5.2.1.2.

Adjust the discharge parameters as described in 5.2.1.3, adjusting first the effective power and, if necessary, the RF voltage.

Optimize the crater shape as described in 5.2.1.4 by adjusting the control parameters. Select the conditions that give an optimally flat-bottomed crater. These conditions are then used during calibration and analysis.

NOTE In order to determine the RF RMS voltage it is essential to include the offset caused by the DC bias voltage, which is not possible to measure at the coupling electrode when non-conductors are sputtered. However, when only thin (<100 µm) non-conductive layers on a conductive specimen are analysed, the offset can be estimated and the amplitude of the RF voltage multiplied by 1,22 can be used as a good estimate of the RMS voltage[18]. For thick non-conductors more complex calculations must be carried out[19]. However, analysis of thick non-conductors is outside the scope of this International Standard.

5.4 Minimum performance requirements

5.4.1 General

The instrument needs to conform to the performance specifications given in 5.4.2 and 5.4.3 below.

NOTE Setting up for analysis commonly requires an iterative approach to the adjustment of the various instrumental parameters described in this International Standard.

5.4.2 Minimum repeatability

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

Perform 10 measurements of the emission intensity on a homogeneous bulk specimen with a content of the analyte exceeding a mass fraction of 1 %. The glow discharge conditions shall be those selected for analysis. These measurements shall be performed using a discharge stabilization time (often referred to as “preburn”) of at least 50 s and a data acquisition time in the range 5 s to 30 s. Each measurement shall be located on a newly prepared surface of the specimen. 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.

5.4.3 Detection limit

5.4.3.1 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 surface layers 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 expected mass fraction in the surface layer to be analysed.

5.4.3.2 SNR method

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

a) Select a bulk specimen to be used as a blank. The composition of the specimen should preferably be similar, in terms of the elemental composition of the matrix, to that of the surface layers to be analysed. Further, the specimen shall be known to contain less than 1 µg/g of the analyte.

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