

FINAL
DRAFT

INTERNATIONAL
STANDARD

ISO/FDIS
14707

ISO/TC 201/SC 8

Secretariat: JISC

Voting begins on:
2020-12-04

Voting terminates on:
2021-01-29

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

*Analyse chimique des surfaces — Spectrométrie d'émission optique à
décharge lumineuse — Introduction à son emploi*

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Reference number
ISO/FDIS 14707:2020(E)

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Published in Switzerland

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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).

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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 third edition cancels and replaces the second edition (ISO 14707:2015), of which it constitutes a minor revision.

The main changes compared to the previous edition are as follows:

- Editorial mistakes have been modified.

A list of all parts in the ISO 14707 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.

Introduction

Glow discharge optical emission spectrometry (GD-OES) is used to determine the elemental composition of solid samples. GD-OES can be used for either bulk or depth profile analysis. In bulk analysis, changes in elemental composition with depth into the specimen are assumed to be negligible. In contrast, the main goal of depth profile analysis is usually to gain information concerning such changes of composition. Layer thicknesses amenable to GD-OES depth profiling range from a few nanometres to approximately one hundred micrometres. An average of the concentration within the crater will be obtained and therefore the lateral resolution of GD-OES corresponds to the inner diameter of the anode.

As is true for any instrumental analysis method, the quality of a GD-OES analysis depends markedly on the correct optimization and operation of the instrumentation. This document provides guidelines of practice that are to be followed to ensure that GD-OES analyses are of the highest possible quality.

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

1 Scope

This document provides guidelines that are applicable to bulk and depth profiling GD-OES analyses. The guidelines discussed herein are limited to the analysis of rigid solids, and do not cover the analysis of powders, gases or solutions. Combined with specific standard methods which are available now and, in the future, these guidelines should enable the regulation of instruments and the control of measuring conditions.

Although several types of glow discharge optical emission sources have been developed over the years, the Grimm type with a hollow anode accounts for a very large majority of glow discharge optical emission devices currently in use both for dc and rf sources. It should be noted, however, that the cathode contact is often located at the back of the sample, in e.g. the Marcus type source, rather than at the front as in the original Grimm design. It should be clearly understood that the guidelines contained herein are equally applicable to both and other source designs and that the Grimm type source is used only as an example.

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 3497, *Metallic coatings — Measurement of coating thickness — X-ray spectrometric methods*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

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*

ISO 5725-3, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

ISO 5725-4, *Accuracy (trueness and precision) of measurement methods and results — Part 4: Basic methods for the determination of the trueness of a standard measurement method*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 3497, ISO 5725-1, ISO 5725-2, ISO 5725-3 and ISO 5725-4 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/>

4 Principle

Analysis by GD-OES involves the following operations:

- a) 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 3 mm, generally 20 mm to 100 mm, are suitable);
- b) atomization and excitation of the analytes to be determined by means of ion sputtering and inter-particle collisions occurring in the glow discharge plasma;
- c) measurement of the emission intensities of characteristic spectral lines of the analytes (for depth profiling, emission intensities are recorded as a function of time);
- d) determination of the analyte concentrations contained in the sample by calibration with reference materials of known composition (for depth profiling, the sputtered depth as a function of time is also determined by calibration with reference materials of known composition and sputtering rates).

A diagram of a typical GD-OES system is presented in [Figure 1](#). GD-OES is based on the use of a glow discharge device as an optical emission source. The glow discharge device consists of a vacuum chamber filled with a supporting gas, usually argon. The glowing plasma, from which the discharge takes its name, is maintained by a controlled high voltage of 200 V to 2 000 V applied between the anode and cathode in the plasma gas. The solid sample to be analysed serves as the cathode.

Atomization of sample material in the glow discharge is the result of cathode sputtering, the destruction of the negative electrode (cathode) in a gas discharge due to the impact of fast charged and neutral particles. Ions formed in the plasma are accelerated toward the cathode surface by the electric field in the plasma. When an ion or neutral atom collides with the surface, its kinetic energy may be transferred to atoms on the surface, causing some of these surface atoms to be ejected into the plasma. Once in the plasma, these sputtered sample atoms may be ionized and excited through inelastic collisions with electrons or other species. The majority of these excited analyte atoms and ions then emit characteristic optical emission upon relaxing into the lower electronic state. The optical emission is analysed by an optical spectrometer containing a dispersive element, normally a diffraction grating. The intensities of element-specific spectral lines are translated to electrical signals by means of appropriate detectors. A polychromator is commonly employed, so that many elements can be quantified simultaneously. Spectral lines that are not contained in the line set of the polychromator can be accessed by means of a scanning monochromator, if one is available. CCD instruments also exist, where a spectrum over a wide spectral range can be measured continuously. In practice almost all elements in the periodic table can be determined, including metals, metalloids and non-metals.

5 Apparatus

At a minimum, the apparatus consists of the following:

5.1 Glow discharge optical emission source

A diagram of a Grimm type glow discharge optical emission device is shown in [Figure 2](#). Several modifications in the device have been introduced by instrument manufacturers. As noted in [Clause 4](#), the sample effectively serves as the cathode. The anode takes the form of a tube with an inner diameter of 1 mm to 10 mm, typically 4 mm. The distance between the front face of the anode and the surface of the cathode is usually between 0,1 mm and 0,3 mm. As a result, ion sputtering is confined to a circular region of the sample surface with a diameter approximately equal to the inner diameter of the anode.

The glow discharge device requires several peripheral pieces of equipment for its operation. These include an electric power supply, one or two vacuum pumps, a source of plasma gas, a means of delivering that gas into the device in a controlled manner and a vacuum gauge. A cooling device, such as a metal block with circulating cooling liquid, is sometimes necessary for thin samples.

- a) Source parameters

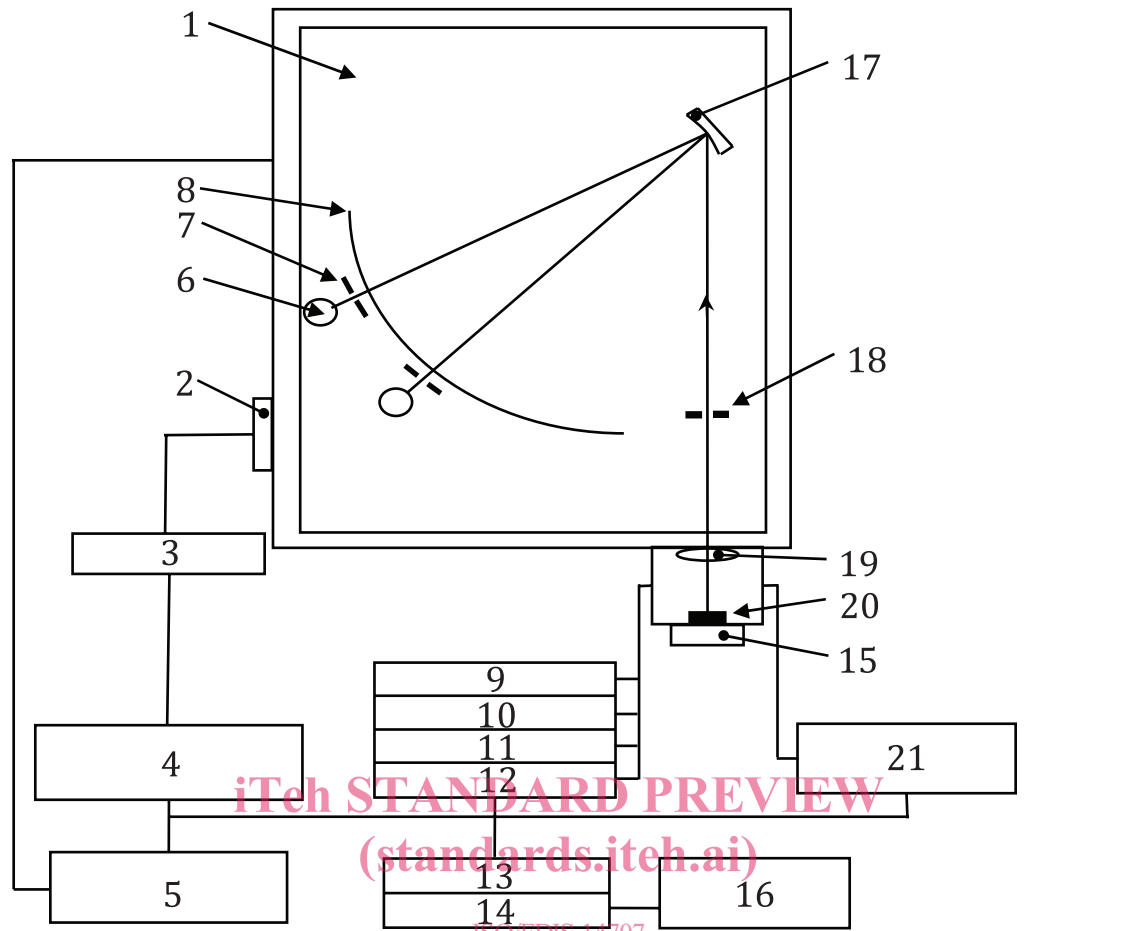
Glow discharge devices may be operated in either direct current (dc) or radio-frequency (rf) mode. Combinations of these two modes, such as the use of an rf voltage superposed onto a dc voltage, have also been reported. In both the dc and rf power modes, a pulsed discharge is also employed for switching the applied power periodically. The following operations shall be conducted with careful attention to safety (see [Annex A](#)):

- 1) For dc operation, the pertinent electrical parameters are discharge current (1 mA to 200 mA) and voltage (200 V to 2 000 V). In addition to the electrical parameters, other parameters are important for the characteristics of the device. These include the inner diameter of the anode (1 mm to 10 mm), gas type and purity (for example, argon, > 99,999 %), gas flow rate or gas pressure introduced (100 ml/min to 500 ml/min, 100 Pa to 1 500 Pa, see note below) and physical characteristics of the sample material (for example, secondary electron emission yield and sputtering yield). The combined effects of all of these factors determine the spectrochemical character of the glow discharge plasma. Generally, it is recommended that the gas flow rate or the gas pressure be varied in real time, in order to achieve constant voltage and current. As an example, typical operating conditions for dc GD-OES bulk analysis of low-alloy steels are 250 ml/min argon flow rate, 600 V to 1 000 V discharge voltage and 20 mA to 60 mA discharge current, for an anode of 4 mm inner diameter. The sputtering rate in this case is typically 100 nm/s varying from 20 nm/s to 160 nm/s for the conditions given in the example.

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Key	https://standards.iteh.ai/catalog/standards/sist/9f76d2cd-3211-4333-a17b-c703a0871af/iso-fdis-14707	
1 spectrometer	8 rowland circle	15 sample
2 electrical lead-in	9 cooling system	16 personal computer system
3 preamplifier	10 gas control system	17 grating
4 light intensity measuring circuit	11 RF power supply	18 entrance slit
5 vacuum/gas flush control system	12 DC power supply	19 lens
6 photomultiplier	13 control circuit	20 glow discharge source
7 exit slit	14 local computer	21 glow discharge control system

Figure 1 — Schematic diagram of a GD-OES system

It should be understood that the discharge gas flow rate is the practical means of controlling the source operating pressure, and so suggested ranges are very much source specific, and are provided here only with reference to the Grimm lamp example.

2) Typical conditions for rf glow discharge include the same range of argon flow rate and similar discharge power and voltage as in dc operation. In terms of the electrical parameters, it is important to note that GD-OES instruments usually measure the forward and reflected power, the applied RMS (root mean square) voltage, or the peak voltage/current of the rf waveform. If conductive samples are sputtered with rf also the average voltage, called dc bias, can be measured. In the power measurement, it shall be understood that the incident power is the forward power delivered to the glow discharge system by the rf power supply. Because of power losses in cables, the cooling system, etc., and the reflected power, caused by an incomplete matching of the generator and plasma impedance, the effective power is lower than the incident power, meaning that the effective power actually dissipated within the glow discharge itself. It is possible to employ a system to automatically measure the power loss as a function of voltage without plasma (under vacuum),

prior to the discharge ignition. This value is then subtracted from the incident power during the measurement, providing a rather accurate measure of the effective plasma power. Similarly, in the measurement of voltage/current, the measured values may not be an accurate representation of the effective discharge voltage/current in the plasma. The rf power supply may be of either the fixed or the variable frequency type. In either case, the rf frequency is usually between 3 MHz and 41 MHz. Common fixed frequencies are 6,78 MHz or 13,56 MHz, in order to comply with national and international regulations.

In addition to conductive samples, rf GD-OES allows the analysis of non-conductive samples. For non-conductive samples, the rate at which ion sputtering erodes the sample surface is usually in the range of 1 nm/s to 50 nm/s. Non-conductive layers may also be examined. For these samples, the applied rf voltage becomes higher than for conductive samples depending on the equipment used.

- 3) In both the dc and rf power modes, a pulsed discharge may be employed to control the sputtering rate and to reduce the damage of surface coatings such as a polymer film. The frequency and the duty cycle of the pulsed discharge should be determined depending on the sample analysed. Typical values for the frequency and the duty cycle are 100 Hz to 300 Hz and 20 %, respectively.

b) Source/spectrometer interface

The optical radiation emitted from excited sample atoms is guided by lenses or mirrors to the entrance slit of the spectrometer. If spectral lines with wavelengths below 200 nm (i.e. vacuum UV) must be used, the entire optical path from the glow discharge source to optical detector must be sufficiently free of molecular oxygen. This is because the oxygen molecule has very strong absorption bands below 200 nm. Oxygen gas can be eliminated from the optical system by flushing the system with a suitable pure gas such as nitrogen (or argon), or by evacuating the optical path to a pressure of ca 1 Pa. The window separating the source and the spectrometer must be cleaned periodically.

5.2 Optical unit

The most common instruments are equipped with a simultaneous spectrometer (for example, polychromator) with several fixed channels corresponding to analyte elements. It is also common to combine this with a sequential spectrometer (i.e. monochromator). With either simultaneous or sequential spectrometers, the spectral bandpass, and thus the effective spectral resolution, is determined by the dispersion of the instrument and the geometrical slit widths.

5.3 Photoelectric detectors and measuring devices

Most glow discharge spectrometers are equipped with photomultiplier tubes for signal detection. To achieve optimum performance (i.e. signal intensity, sensitivity and detection limit), photomultipliers with low dark current and high quantum efficiency are required. The photomultiplier gain shall be selected properly to avoid nonlinear response and saturation. This is accomplished by measuring selected samples containing different analyte concentrations and sputtering rates and adjusting the gain in such a way that sufficient sensitivity at the lowest intensities is ensured, without saturation of the detector at the highest intensities. An array-type detector, such as a charge coupled device (CCD) or a charge injection device (CID), is also used for simultaneous detection to cover a wide spectral range of the analytical lines. The amplified detector output is digitized by means of analog-to-digital converters and transferred to a computer for data storage and further evaluation.

6 Procedure

6.1 Verification tests of apparatus

6.1.1 General

In order to obtain analytical data of the highest possible quality, it is necessary to verify the performance of the spectrometer and all devices connected to the system. If such verification was not performed by