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Low alloyed steel — Determination of C, Si, Mn, P, S, Cr, Ni, Al, Ti and Cu - Glow discharge optical emission spectrometry (routine method)

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National foreword

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Foreword

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The committee responsible for this document is ISO/TC 17, *Steel*, Subcommittee SC 1, *Method of determination of chemical composition*.

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Low alloyed steel — Determination of C, Si, Mn, P, S, Cr, Ni, Al, Ti and Cu - Glow discharge optical emission spectrometry (routine method)

1 Scope

This International Standard specifies a glow discharge optical emission spectrometric (GD-OES) method for determination of the mass fraction Carbon, Silicon, Manganese, Phosphorus, Sulfur, Chromium, Nickel, Aluminium, Titanium and Copper in low alloyed steels.

The content ranges to which the method is applicable are shown in Table 1.

Table 1 — Content ranges

Element	Content ranges mass fraction %
C	0,060 to 0,35
Si	0,14 to 1,50
Mn	0,090 to 0,70
P	0,010to 0,070
S	0,005 to 0,050
Cr	0,008 to 0,65
Ni	0,050 to 0,50
Al	0,006 to 0,90
Ti	0,014 to 0,13
Cu	0,005 to 1,00

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable to 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 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 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*

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3 Principle

The method used involves the following steps:

a) a sample with a flat and smooth surface is used as the cathode of a direct current or radio frequency glow discharge device;

b) cathodic sputtering of the sample surface, atomization of the sputtered atoms and ions from the sample surface; excitation of these atoms and ions in the plasma formed in the glow discharge device;

c) spectrometric measurement of the intensity of the emitted light from the ions or the atoms of the elements to be determined and, optionally, the emitted light from iron at 371,994 nm or 271,441 nm or another appropriate wavelength (if internal standard is used);

d) conversion of the measured signals to the contents through calibration curves established by measuring certified reference materials.

4 Apparatus

4.1 Glow discharge optical emission spectrometer

4.1.1 General

An optical emission spectrometer system consists of a Grimm type or similar glow discharge source (direct current or radio frequency powered) and a simultaneous optical spectrometer as described in ISO 14707, with suitable spectral lines for the elements to be determined. A sequential optical system may also be used alone or combined with simultaneous channels.

A 2 mm to 8 mm range of the inner diameter of the anode of the glow discharge is recommended. A cooling device is also recommended, but not strictly required for implementation of the method. The anode-cathode gap is normally around 0,1 mm to 0,3 mm; otherwise, follow the instrument manufacturer's instructions.

4.1.2 Short term stability

Carry out at least 10 measurements of the emission intensity of an element having a content around the corresponding upper limit specified in this International Standard on an appropriate sample. Allow the discharge to stabilize for at least 50 s before each measurement. The data acquisition time should be in the range of 5 s to 30 s. Each measurement shall be carried out on a newly polished surface of the sample. Calculate the corresponding standard deviation and mean. The relative standard deviation (RSD) should not exceed 5 % for contents less than 0,5 %, otherwise, the RSD should not exceed 3 %.

4.1.3 Detection limit

Detection limits may be determined by either the SNR method or SBR-CVB method (see A.1 and A.2).

4.1.4 Data acquisition and processing system

The data acquisition and processing system is conducted by a computer, equipped with software suitable for controlling the instrument parameters and running the test programs.

4.1.5 Others

For other basic requirements of the instrument, use ISO 14707.

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5 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for steel.

6 Procedure

6.1 Sample preparation

Samples shall be homogeneous, flat and free of porosity. The surface of the sample shall be prepared by using suitable methods to ensure cleanliness and flatness. Surface preparation may be achieved by using abrasive-wheel or milling machine. All the reference materials and samples shall be prepared under the same conditions and their size should be suitable for the glow discharge source used.

6.2 Selection of spectral lines

For each element to be determined, there are a number of spectral lines that can be used. Suitable lines shall be selected on the basis of several factors, including the spectral range of the spectrometer used, element concentration, sensitivity of the spectral lines and spectral interference from other elements present in the samples. Table 2 contains some suggestions concerning suitable spectral lines. With these lines, no obvious inter-element interferences are observed in low alloyed steels. Spectral lines other than those listed may be used, if they have favourable characteristics, but special attention needs to be paid to the influence of co-existing elements and corrections might be required.

Table 2 — Suggested wavelengths for the analysis of low alloy steels

Element	Wavelength nm
Fe	371,994
	271,441
C	165,700
	156,143
Si	288,158
	251,611
Mn	403,449
	257,610
P	177,497
	178,287
S	180,731
Cr	425,433
Ni	349,296
	341,477
Al	396,152
Ti	337,279
	365,350
Cu	219,228
	327,396

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6.3 Optimization of the instrument

6.3.1 General

Follow the manufacturer's instructions or other suitable documented procedures to start and set the GD-OES and let it stabilize. Check, or adjust if necessary, the entrance slit in accordance with the manufacturer's instructions to ensure it is correctly positioned so that the intensity is measured at the peak of the spectral line in order to obtain the best signal to background ratio (make reference to ISO 14707 for further information). Carry out at least three preliminary discharges on a generic sample before any measurement procedures.

NOTE Analyte lines are centred by adjusting the entrance slit whilst carrying out discharges on a reference material. It is advisable to profile the instrument on a daily basis for a newly installed instrument during the first week of operation and then periodically over time. Profiling is carried out initially on all lines or at least on those included in each analytical program or by following the recommendations of the instrument manufacturer.

Follow manufacturer's recommendation or other suitable documented procedures to select or adjust all instrumental parameters: evacuation time, argon purging time [pumpdown cycles], glow discharge spectrometer opening mode [startup time], flush time [cleaning time], sputtering time, etc.

6.3.2 Setting the discharge parameters of a direct current (DC) source

DC glow discharge spectrometers usually have three parameters (current, voltage and pressure) to be controlled. Any two of these three parameters may be fixed to constant values by varying the third one. The user may adopt the following procedures, or any other mode recommended by the manufacturers.

6.3.2.1 Constant applied voltage and current

The controlled parameters are applied voltage and current. Set the power supply of the glow discharge source to constant voltage and constant current operation. Firstly, set the voltage and current to typical values recommended by the manufacturer or reliable values. If the recommended values are not available or not suitable for the task, following steps could be pursued to determine the optimum parameters.

Set the high voltage of the detectors as described in 6.3.4.

Step one: set an initial value or the value recommended by the manufacturer for current and voltage (initial discharge condition). For DC glow discharge, electrical current is normally in the range of 5 mA to 10 mA for a 2 mm to 2,5 mm anode, 15 mA to 45 mA for a 4 mm anode and 40 mA to 100 mA for a 7 mm to 8 mm anode. Voltage is usually in the range of 600 V to 1250 V. Determine the intensities corresponding to an appropriate sample under the initial discharge condition. Fix one parameter (current or voltage), and change the other one gradually. Measure the intensities at least seven times at each setting. Do this at the entire parameter range allowed by the instrument.

Step two: fix the parameter which changed in step one and gradually change the other parameter. Repeat the operation as described in step one.

Step three: calculate the CVs of the measurements for each setting. Investigate the influence of the discharge parameters on the intensities and CVs and fix the optimum instrumental condition.

6.3.2.2 Constant applied current and pressure

The controlled parameters are applied current and pressure. Set the power supply of the glow discharge source to constant current and constant pressure operation. Firstly, set the current and pressure to typical values recommended by the manufacturer or values suitably documented. If the recommended values are not available or not suitable for the task, the following steps could be pursued to determine the optimum parameters.

Set the high voltage of the detectors as described in 6.3.4.

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Step one: set an initial value or the value recommended by the manufacturer for current and pressure (initial discharge condition). For DC glow discharge, electrical current is normally in the range of 5 mA to 10 mA for a 2 mm to 2,5 mm anode, 15 mA to 45 mA for a 4 mm anode and 40 mA to 100 mA for a 7 mm to 8 mm anode. Set the initial pressure to a value to obtain a voltage in the range of 600 V to 1250 V or set the initial pressure to a value which is in the middle of the allowed range of the instrument. Determine the intensities corresponding to an appropriate sample under the initial discharge condition. Fix one parameter (current or pressure) and change another one gradually. Measure the intensities at least seven times at each setting. Do this at the entire parameter range allowed by the instrument.

Step two: fix the parameter which changed in step one and gradually change the other parameter. Repeat the operation as described in step one.

Step three: calculate the CVs of the measurements for each setting. Investigate the influence of the discharge parameters on the intensities and CVs and fix the optimum instrumental condition.

Use a similar procedure to optimize the analytical parameters for other operation modes.

6.3.3 Setting the discharge parameters of radiofrequency (RF) source

At the time of publication of this International Standard, most RF sources are operated with constant applied power and constant pressure. Other modes also exist such as:

— constant applied power and constant voltage;

— constant voltage and constant pressure;

— constant power and constant argon flow, etc.

All RF operational modes are allowed in this International Standard, provided they meet the requirements described in 4.1.2 and 4.1.3 and ensure that constant excitation conditions in calibration and analysis can be kept for optimum accuracy.

6.3.3.1 Constant applied power and pressure

The controlled parameters are applied power and pressure. Set the power supply of the glow discharge source to constant power and constant pressure. First set the power and pressure to typical values recommended by the manufacturer or values suitably documented. If the recommended values are not available or not suitable for the task, following steps could be pursued to determine the optimum parameters.

Set the high voltage of the detectors as described in 6.3.4.

Step one: set an initial discharge condition which may be the value recommended by the manufacturer or a value in the middle of the parameter range allowed by the instrument for power and pressure. Determine the intensities corresponding to an appropriate sample under the initial discharge condition. Fix one parameter (power or pressure) and change the other one gradually. Measure the intensities at least seven times at each setting. Do this at the entire parameter range allowed by the instrument.

Step two: fix the parameter which changed in step one and gradually change the other parameter. Repeat the operation as described in step one.

Step three: calculate the CVs of the measurements for each setting. Investigate the influence of the discharge parameters on the intensities and CVs and fix the optimum instrumental condition.

6.3.3.2 Constant power and voltage

The controlled parameters are applied power and voltage. Set the power supply of the glow discharge source to constant power and constant voltage. First set the power and voltage to typical values recommended by the manufacturer or values suitably documented. If the recommended

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values are not available or not suitable for the task, following steps could be pursued to determine the optimum parameters.

Set the high voltage of the detectors as described in 6.3.4.

Step one: set an initial discharge condition which may be the value recommended by the manufacturer or a value in the middle of the parameter range allowed by the instrument for power and voltage. Determine the intensities corresponding to an appropriate sample under the initial discharge condition. Fix one parameter (power or voltage) and change the other one gradually. Measure the intensities at least seven times at each setting. Do this at the entire parameter range allowed by the instrument.

Step two: fix the parameter which changed in step one and gradually change the other parameter. Repeat the operation as described in step one.

Step three: calculate the CVs of the measurements for each setting. Investigate the influence of the discharge parameters on the intensities and CVs and fix the optimum instrumental condition.

Use a similar procedure to optimize the analytical parameters for other operation modes.

6.3.4 Optimization of the detection system

Photomultiplier power input shall be selected as a function of the type of detector and the content range of each element to be determined. Operate the source and observe the output signals from the detector of the elements concerned, adjust the high voltage of the detectors in such a way that sufficient sensitivity at the lowest analyte concentrations is ensured, without overflowing the detectors at the highest analyte concentrations.

6.3.5 Pre-burning time and integration time

After a glow discharge is initiated, it needs some time to reach stabilization. This stabilization time is dependent on the conditions of the instrument and sample surface. Measurement of the signals can only be done after stabilization. This requirement is met by setting a suitable pre-burning time. A pre-burning time reasonably set may also clean the sample surface to eliminate a possible contamination caused by sample preparation.

Select pre-burning time according to the manufacturer's recommendation. If the recommended value is neither suitable nor available, select it as described below:

Excite the sample continuously, record the diagram of intensity vs sputtering time. Select a sputtering time, at which the intensity became sufficiently stable, as pre-burning time.

Select integration time according to the manufacturer's recommendation. If the recommended value is neither suitable nor available, select it as described below:

Set a series of integration times, normally in the range of 5 s to 50 s. Measure the intensities corresponding to the elements to be determined at least seven times at each integration setting. Check the influence of the integration times on intensities and CVs. Integration time shall be long enough to ensure CVs required in 4.1.2.

6.3.6 Validation of the instrumental parameters

The discharge parameters and detector high voltages selected shall be used for the analytical program. Using a suitable sample, carry out some preliminary tests and ensure that the key instrumental parameters are appropriate to meet the criteria described in 4.1.2 and 4.1.3.

6.4 Calibration

A series of certified reference materials (CRM) (at least five for each element), which have the same or at least very similar matrix and metallurgical structure as the samples to be analysed is used to prepare the calibration curves. The content range of the CRM used shall cover that of all the samples to

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be analysed within each specific analytical program. Adjust the source parameters as described in 6.3. Measure each CRM at least three times and every time on a new area of the sample surface. The mean intensity is correlated to the corresponding certified content and a regression is calculated by the least squares method. In order to minimize possible signal fluctuations, it is advisable to use the internal standard method.

6.5 Checking of the trueness of the method

In order to check the trueness of the method, select a series of certified reference materials, necessarily independent from that used for the calibration of the spectrometer and analyse it. The composition of the certified reference materials selected shall cover the full range of the calibration. The results obtained for each certified reference material shall be situated in the interval "Certified Value ± 2σ", where σ is standard deviation of certified value.

If necessary, in order to fulfil this trueness requirement for all the certified reference materials analysed, carry out adjustments of the calibration curves (inter element corrections and/or modification of the mathematical function defining each curve). If the trueness criteria cannot be reached, re-prepare the calibration curve or re-select the parameters.

6.6 Drift correction

Before starting a series of determinations by using an already recorded program, it's necessary to check the drift condition of the instrument. The procedure for drift checking is the same as described in 6.5. Drift correction is not necessary if the results are within specified accuracy; otherwise, the drift correction shall be carried out.

Whenever the drift correction is performed, an accuracy control needs to be carried out as described in 6.5.

6.7 Analysis of the samples

Each sample shall be analysed at least three times. Use the mean intensity to derive the content of each element from the corresponding calibration curve.

In the case where the internal standard method is employed, use the intensity ratio between each analyte and the internal standard element.

The content of each element to be determined shall be within the range of the calibration curves.

7 Expression of results

7.1 Method of calculation

Using the intensities (or intensity ratios) obtained, the content of each element measured, expressed as mass fraction, is derived from the calibration curves established in 6.4.

7.2 Precision

A planned precision trial of this method was carried out by 11 laboratories, at 19 content levels for Carbon, Silicon and Manganese, 21 for Phosphorus and Chromium, 22 for Sulfur, 18 for Nickel, 15 for Aluminium and Titanium and 23 for Copper. Each laboratory made three determinations for each element at each level.

NOTE 1 Two of the three determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

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