SLOVENSKI STANDARD
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Analiza z optično emisijsko spektrometrijo malolegiranega jekla (rutinska metoda) - Vodilo za pripravo standarda za rutinsko metodo z optično emisijsko spektrometrijo

Optical emission analysis of low alloy steels (routine method) - Guidelines for the preparation of standard routine method for optical emission spectrometry

Analyse des aciers faiblement alliés par spectrométrie d'émission optique (méthode de routine) - Lignes directrices relatives a la préparation d'une méthode normalisée de routine pour la spectrométrie d'émission optique

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EUROPEAN COMMITTEE FOR STANDARDIZATION
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Contents

Foreword

This CEN Report has been prepared by Technical Committee ECISS/TC 20 "Methods of chemical analysis of ferrous products", the secretariat of which is held by SIS.

1 Scope and field of application

The purpose of this document is to describe concepts and procedures for calibration and analysis of the equipment based on spark source optical emission spectrometry. Optical emission spectrometers are equipments that provide a quality and quantity characterization of electromagnetic radiation which is emitted by a test sample when excited by a suitable source.

2 Terms and definitions

For the purposes of this CEN Report, the following definitions apply:

2.1
absolute error
the difference between the measured and the true value

2.2
accuracy
the closeness of agreement between an observed value and an accepted true value

2.3
analyte line
the spectral line of an element which is used to establish the element concentration

2.4
background equivalent concentration
the quantity of analyte which, when subjected to excitation, provides a net intensity equal to the spectral background

2.5
calibration
the series of operations which, under specified conditions, establishes the relationship between the instrument output and the known values of the element being determined

2.6
calibration curve
the mathematical or graphical relationship between instrument output and known values of an element, under given conditions

2.7
certified reference material
a reference material whose properties are certified by a technically valuable procedure and which is provided with a certificate, either attached or referenced, issued by a certification body

2.8
drift
a slow change over time in instrument response

2.9
instrumental drift correction
the correction of instrumental drift with time, in order to keep calibration constant

2.10
limit of detection
the minimum concentration at which the signal generated by a given element can be positively recognised above any background signals with a specified degree of certainty

2.11
matrix
the sum of the principal elements in a sample

2.12
matrix effect
the effect of the main constituents of a spectrographic sample on the intensity of the analyte line of the element being measured

2.13
nominal value
the value used to indicate a characteristic of a reference material

2.14
primary standard
a standard showing the best metrological properties in a specified field

2.15
random error
the component of an error of measurement which, during several measurements of the same measurand, changes with an unknown pattern

2.16
reference material
a material or substance which has sufficiently defined properties to be used for the following purposes: calibrate an instrument, evaluate a measuring system or assign values to other materials

2.17
reference standard
a standard, generally with the best metrologic properties available at a certain location, which is used for the metrological measurements performed at that location

2.18
relative error
the absolute error divided by the true value

2.19
repeatability
the value within which the absolute difference between two single test results obtained with the same method in the shortest possible time by the same operator, using the same apparatus, at the same calibration values and under the same drift conditions may be expected to lie within a specified probability (95 % if not indicated)

2.20
reproducibility
the value below which the difference between two single test results obtained with the same method on the same material by different operators using different instruments at different laboratories and at different times may be expected to lie within a specified probability (95 % if not indicated)

2.21
secondary standard
a standard whose value is established by comparison with a primary standard

2.22
span
the magnitude of the difference between two limits in the nominal range of an instrument

2.23
specified working range
range of values of an element for which instrumental errors are within acceptable limits

2.24
spectral line
the characteristic line emitted by an element during the electronic transition from the excited state to the ground state

2.25
systematic error
the component of an error of measurement which, during several measurements of the same measurand, remains constant or changes with a known pattern

2.26
true value
the value which characterizes a perfectly defined quantity in the conditions which exist at the moment when the quantity is observed

2.27
uncertainty of measurement
an evaluation of the range of values within which the true value lies

3 Basic principles of optical emission spectrometry

If a sufficient amount of energy is applied to an atomized gas, the gas atoms "are excited", i.e. they emit a radiation with a characteristic wavelength. It is thus possible to obtain an emission spectrum where each line corresponds to a quantum jump or a transition from a given energy level to a lower one, whose value is known. Each atom is characterized by a series of possible energy levels. Therefore, if suitably excited, an atom produces a typical emission spectrum. The intensity of spectral lines depends both on how likely transition is and the number of atoms involved. Since the portion of excited atoms relates to the total number of atoms of the same element which are present in the test sample, it is possible to establish, within certain limits, a relationship between the intensity of the electromagnetic radiation emitted and the quantity of atoms present. By a suitable adjustment it is also possible to correlate intensity to quantity and execute quantitative measurements.

Usually a single equipment is used to atomize, or better vaporize in atomized form, the substance under test and to excite the atomic gas thus obtained. The simplest way to excite the gas is heating a substance by direct contact with a flame. The first excitation source used for spectrometry has been flame, since this is particularly suitable to excite alkaline substances, for which purpose it is still used. Electric arc and spark are used to achieve higher temperatures and excite a larger number of elements. Optical emission spectrometers, either simultaneous or sequential, encompass all these features. They are used on a large scale in the steelmaking industry and more generally in the metallurgical industry for production control.

4 Apparatus

An optical emission spectrometer is composed of:

a) a source for excitation;

b) an optical system;

c) a detector;

d) one or more reading instruments;

e) hardware and software management system.

A source is the system which provides the necessary excitation energy to be applied to the test sample. The source referred to in this standard is a thermal excitation source. This type of source excites the sample by raising its temperature, so that the shock among high-kinetics atoms produces an electronic jump from the ground state to the excited one. The most common source is an electronic arc. The test sample, that acts as a cathode, excites and produces plasma which emits raditations over a wide range of wavelengths (from distant IR to vicinal UV). A suitable multi-channel spectrometer resolves radiations into their respective wavelengths. Among these, analyte lines (1 to 3 in number) are selected for each element to reach the multi-channel spectrometer either simultaneously or one by one. Each electromagnetic radiation is then processed by the detection system, a photomultiplier, and transformed into a measurable electronic signal.

Plasma electromagnetic radiations are emitted by both gas atoms and test sample atoms.

The task of the hardware is to check instrument parameters while the software processes data (for example, entry and control of the electronic signal coming from photomultipliers, selection of suitable signal amplification scales, etc.).

4.1 Source

The source provides the energy necessary to release solid-state atoms and gives them the speed required to get sufficient energy for transition at the subsequent emission of characteristic radiations.

In a spark, the discharge between two electrodes is not continuous, rather it is composed of a series of very short damped oscillatory discharges at a constant frequency (50 Hz single-frequency) or high (50 Hz to 1 KHz multi-frequency) and very high peak voltages (> 15 kV). These ohmic drops generate almost instantaneous (some hundredths of a second) voltaic arcs that make the test sample sublimate with consequent generation of a thick plasma and emission of electromagnetic radiations.

4.1.1 Technical features

The atomization and spark-excitation system is composed of a generator that operates at low or high voltage according to test material conductivity. The generator includes a transformer, a condenser, an inductance and a synchronous initiator. Operating conditions depend on the type of source and material conductivity. In general, the parameters that determine the analytical conditions of a discharge are as follows:

a) voltage;

b) inductance;

c) resistance;

d) capacitance;

e) frequency;

f) flow rate;

g) pre-discharge rate;

h) integration rate.

The sample discharge strikes in an argon atmosphere at a flow rate that is a function of both test sample and source conditions. It is necessary that the analysis is carried out in the absolute absence of oxygen. The position and cleanliness of the electrode are also important factors for a good discharge. The frequency of electrode cleaning and repositioning depends on test conditions and type of test sample.

4.2 Optical system

In emission spectrometry two types of optical systems are mainly used:

1) optical system with monochromator;

2) optical system with polychromator.

The former is used for sequential analysis, the latter to measure several spectral lines simultaneously. Optical system can operate under vacuum (10-5 m barr), with inert flow or in pressure. Inert gas does not absorb the radiations that correspond to the analyte lines provided on the instruments, particularly when the spectral band used is below the wavelength (190 nm) of oxygen interference. The optical system shall have a high resolution (0.01-0.02 nm) and an absence of diffused light. The function of the optical system is to transfer, disperse and select the light emitted by the excited sample. Its components are:

a) lens or mirror assembly;

b) a monochromator or polychromator;

c) a focal plane.

4.2.1 Lens assembly

A biconvex lens, sometimes a simple slit only, is placed between the excitation stand and the monochromator (or polychromator) to focus the emitted light onto the collimator.

4.2.2 Monochromator

A monochromator is a complex dispersion system composed of:

a) a radiation entry slit;

b) a collimator;

c) a dispersing element (a grating and/or a prism);

d) an exit slit for the selection of electromagnetic radiation spectral bands.

Width and height of entry slits can be changed continuously or stepwise, according to the range of wavelengths and spectral factors of transmission.

The collimator parallels the radiation beam coming out from the exit slit.

The dispersing element resolves the light beam. The properties of the dispersing element are expressed as resolution, which is affected by various factors, such as:

a) dispersion;

b) slit width;

c) quality of components.

In modern spectrometers the dispersing element is a grating, rarely combined with a prism.

The monochromator selects a band pass of a wavelength at a time, thus to analyse the spectrum it is necessary adequately to change the angle of incidence between the dispersing element and the radiation.

4.2.3 Polychromator

The polychromator is composed of:

a) a main slit;

b) lens and mirror assembly for primary radiation focus;

c) a dispersing element;

d) secondary slits near the photomultiplier.