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Replacing GB/T 4336-2002

Carbon and low-alloy steel - Determination of multi-element contents - Spark discharge atomic emission spectrometric method (routine method)

碳素钢和中低合金钢 多元素含量的测定

火花放电原子发射光谱法（常规法）

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Foreword

This Standard is drafted in accordance with the rules given in GB/T 1.1-2009.

This Standard replaces GB/T 4336-2002 “Carbon and low-alloy steel - Spark discharge atomic emission spectrometric method (routine method)”, compared with GB/T 4336-2002, main technical content changes are as follows:

- The standard name is changed to “Carbon and low-alloy steel - Determination of multi-element contents - Spark discharge atomic emission spectrometric method (routine method)”;

- MODIFY the measurement range of each element in Table 1;

- ADD the reference in “2 Normative references”;

- MODIFY the description of the principle in “3 Principle”;

- MODIFY the description of the excitation light source in 4.1;

- MODIFY the description of the spark room in 4.2;

- MODIFY the requirements for the purity of argon in 4.3, clearly specify the argon pressure and the instrument parts with constant flow;

- MODIFY the description of the electrode in 4.4;

- MODIFY the focal length and wavelength range in 4.5;

- MODIFY the description of the photometric system in 4.6;

- MODIFY “6 Standard samples and recalibrated samples” TO “6 Standard samples, standardization samples and control samples”; MODIFY the corresponding description;

- ADD “8 Calibration” and its description;

- MODIFY “8 Analysis conditions and analysis procedures” TO “9 Analysis conditions and analysis procedures”; MODIFY its description;

- MODIFY “10 Precision” TO “11 Precision”; re-calculate the repeatability limit and reproducibility limit formulas of each element according to the results of precision test;

- ADD “12 Acceptability of measurement results and determination of final report result";

Carbon and low-alloy steel - Determination of multi-element contents - Spark discharge atomic emission spectrometric method (routine method)

1 Scope

This Standard specifies the determination of carbon, silicon, manganese, phosphorus, sulfur, chromium, nickel, tungsten, molybdenum, vanadium, aluminum, titanium, copper, niobium, cobalt, boron, zirconium, arsenic and tin contents in carbon and low alloy steels by spark discharge atomic emission spectrometric method (routine method).

This Standard applies to the sample analysis of casting or forging carbon and low-alloy steels by electric furnace, induction furnace, electroslag furnace, converter furnace, etc.; see Table 1 for the measurement range of each element.

Table 1 Determination range of each element

Element	Measurement range (mass fraction)/%
C	0.03～1.3
Si	0.17～1.2
Mn	0.07～2.2
P	0.01～0.07
S	0.008～0.05
Cr	0.1～3.0
Ni	0.009～4.2
W	0.06～1.7
Mo	0.03～1.2
V	0.1～0.6
Al	0.03～0.16
Ti	0.015～0.5
Cu	0.02～1.0
Nb	0.02～0.12
Co	0.004～0.3
B	0.000 8～0.011
Zr	0.006～0.07
As	0.004～0.014
Sn	0.006～0.02

2 Normative references

The following documents are indispensable for the application of this document. For dated references, only the dated edition applies to this document. For undated references, the latest edition (including all modifications) applies to this document.

GB/T 6379.1 Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions

GB/T 6379.2 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

GB/T 20066 Steel and iron - Sampling and preparation of samples for the determination of chemical composition

3 Principle

Discharge is generated between the prepared bulk sample and the counter electrode under the action of the spark light source, and the plasma is generated in the high temperature and the inert atmosphere. When the atoms of the measured element are activated, the electrons are transitioned between different energy levels in the atom, and the characteristic spectrum is generated when the transition from the high-energy level to the low-energy level. Measure the spectral intensity of the characteristic spectrum of the selected analytical element and the internal standard element. According to the relation between the spectral intensity (or intensity ratio) and the concentration of the element to be measured in the sample, the content of the element to be measured is calculated by the calibration curve.

4 Instruments

The spark discharge atomic emission spectrometer consists mainly of the following units.

4.1 Excitation light source

The excitation light source shall be a stable spark excitation light source.

4.2 Spark room

The spark room is specially designed for use with argon, and the spark room is mounted directly on the spectrometer, with an argon flush spark bracket to place the flat sample and the rod-shaped counter electrode. The argon gas path in the spark

results, 1 ~ 2 samples are used to standardize the instrument, these samples are called standardization samples. The sample shall be very uniform and have an appropriate content; the sample can be selected from standard samples or specially smelted. When using two-point standardization, the content is the content on each element calibration curve, respectively, near the upper and lower limits.

The standardization sample is used to correct the deviation of the measured value of the instrument from the calibration curve due to various causes. The standardization sample shall be uniform and capable of obtaining a stable spectral line intensity.

6.3 Control samples

The control sample is the uniform sample with similar metallurgical process, organizational structure and chemical composition to those of the analytical sample, being used for correcting the measurement results of the analytical sample or for type standardization correction.

The control sample can be made by molding of molten metal or from metal products; when smelting the control sample, the content of each element shall be specified appropriately, so that the matrix composition of each sample is roughly equal; when assigning the control sample, attention shall be paid to the setting error of standard values and the traceability of data and methods.

7 Preparation of instruments

7.1 Storage of instruments

The spectrometer, as recommended by the equipment manufacturer, shall be placed in shock-proof and clean laboratories, usually the indoor temperature maintains at 15 °C ~ 30 °C and the relative humidity shall be less than 80 %. In the same standardization cycle, the indoor temperature change does not exceed 5 °C.

7.2 Power supply

To ensure the stability of the instrument, the power supply voltage change shall be less than ± 10 %, the frequency change shall be less than ± 2 % and the AC power supply shall be the sine wave. According to the use requirements of the instrument, a dedicated ground line shall be equipped.

7.3 Excitation light source

In order to make the electrical part of the excitation light source work stably, before starting work, it shall be given the appropriate power time.

Use a voltage regulator or a voltage regulator device to adjust the power supply voltage

to the desired value of the instrument.

7.4 Counter electrode

The electrode shall be regularly cleaned and replaced, the distance of the analysis gap shall be adjusted with the distance gauge, to keep it in normal working condition.

7.5 Optical system

The condenser shall be regularly cleaned and traced to correct the entrance slit position.

7.6 Photometric system

After being shut down and then restarted, generally adequate power time shall be endured to make the photometric system work stably.

Select the appropriate pre-combustion time of the analytical element by making a pre-combustion curve. The integration time is determined by the test basing on the analytical accuracy.

8 Calibration

8.1 Calibration curve method

Under the selected working conditions, activate a series of standard samples; in principle, use the standard samples of more than 5 levels, and activate at least 3 times per sample; plot a curve indicating the relation between the luminous intensity (or intensity ratio) and the content (or content ratio) of the analytical element as a calibration curve. Use this calibration curve to measure the element content in the sample.

8.2 Original calibration curve method

The original calibration curve method is to use the calibration curve method to plot the calibration curve. When temperature, humidity, vibration and other factors lead to displacement of the spectral line of the spectral instrument, or changes in luminous intensity leads to the calibration curve drifts, use the standardization sample to correct the drift of the calibration curve, to resume the strength of the corrected element to the strength when the calibration curve is initially established.

8.3 Control sample method

Due to the difference in the smelting process and the organizational structure between the analytical sample and the standard sample used to plot the calibration curve, the calibration curve is often changed. To avoid the effects of this difference, the control

9.2.2, each sample is activated at least 2 times (the sample is activated once to obtain an independent measurement result; and activate once at the opposite position of the activating point of the sample to obtain the second independent measurement result). According to the requirements of Clause 12, determine the acceptability of the measurement results and determine the final report result.

10 Calculation of analysis results

According to the relative strength (or absolute intensity) of the analytical line, obtain the content of the analytical element from the calibration curve.

The analysis result of the elements to be measured shall be within the content range of a series of standard sample used for the calibration curve.

11 Precision

The precision test of this Standard has been carried out by 15 laboratories to 11 to 22 levels of 14 elements in low-alloy steels in 2013, and by 12 laboratories to 18 to 36 levels of 5 elements in low-alloy steels in 2014. Under the repeatability condition as specified in GB/T 6379.1, each laboratory shall measure the content of each level of element 2 times.

The samples used are listed in Tables A.1 to A.19 of Annex A.

According to GB/T 6379.2, statistically process the result obtained. The function relation between the content of each element and the reproducibility limit, *r*, and the reproducibility limit, *R*, of the test result is summarized in Table 4.

measurement results (measure for one or two more results)

13 Determination of the accuracy of laboratory measurement results

Under the reproducibility conditions, a laboratory measures the standard sample and obtains two independent measurement results, and the arithmetic mean, $\bar{x}$, is compared with the determined value μ_0. At 95 % probability level, the critical difference, $CD_{0.95}$, of $|\bar{x} - \mu_0|$ is calculated according to formula (1):

$$CD_{0.95} = \frac{1}{\sqrt{2}}\sqrt{R^2 - r^2/2} \quad \text{..... (1)}$$

When the uncertainty, U, of the standard sample is not negligible, the critical difference, C, of $|\bar{x} - \mu_0|$ is calculated according to formula (2)

$$C = \sqrt{CD_{0.95}^2 + U^2} \quad \text{..... (2)}$$

In this Standard, the repeatability limit, r, the reproducibility limit, R, the standard deviation limit, s, of 10 measurements, and the critical difference, $CD_{0.95}$, between the mean, $\bar{x}$, and the determined value, μ_0, of each element to be measured of different contents are listed in Tables B.1 to B.19 in Annex B.

14 Test report

The test report shall include the following contents:

a) all the information required for identifying samples, laboratories and test dates;

b) the reference standard;

c) the results and their representations;

d) the analytical line used;

e) the anomalies found in the measurement;

f) various operations or optional operations that are not specified in this Standard and have had an impact on the results.

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