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Analytical methods of metallurgical products – General rule for X-ray fluorescence spectrometric methods

冶金产品分析方法 X 射线荧光光谱法通则

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Analytical methods of metallurgical products – General rule for X-ray fluorescence spectrometric methods

1 Scope

This standard specifies the general requirements for quantitative analysis of elements by X-ray fluorescence spectrometry, including terms and definitions, basic principles, instruments, reagents and materials, preparation methods of samples, quantitative analysis, safety precautions, records and expression of measurement results.

This standard applies to wavelength dispersive and energy dispersive X-ray fluorescence spectrometers, to measure the element composition and element content in various materials. It can be used for qualitative and quantitative analysis of constant and trace of all elements from $_{4}Be$ to $_{92}U$ in the periodic table, in addition to H, He, Li, for wavelength dispersive and energy dispersive X-ray fluorescence spectrometers, which use X-ray tubes as excitation sources. The mass fraction range of the analyzed elements: 0.0001% ~ 100%.

2 Normative references

The following documents are essential to the application of this document. For the dated documents, only the versions with the dates indicated are applicable to this document; for the undated documents, only the latest version (including all the amendments) is applicable to this standard.

GB/T 6379.2 Accuracy of measurement methods and results (trueness and precision) - Part 2: Basic methods for determining the repeatability and reproducibility of standard measurement methods

JJG 810 Wavelength dispersive X-Ray fluorescence spectrometers

3 Terms and definitions

The following terms and definitions apply to this document.

3.1

X-ray intensity

The count of intensity in X-ray fluorescence spectroscopic analysis per unit time, the fluorescent X-rays, which are emitted by the sample. The position of the analyzing crystal is controlled by a transmission mechanism, that can maintain the angle reproduction accuracy for a long time; the material of the analyzing crystal is required to be less affected by temperature changes and to be stable for a long time.

5.1.6.4 Detectors

The X-ray photon energy is converted into a pulse proportional to the energy; the detector has a proportional characteristic of identifying energy. Commonly used detectors include semiconductor counters, flow-type proportional counters (flow-type or closed), scintillation counters.

5.1.7 Counting-recording systems

Select the desired pulses from the output pulses of the detector to count; display and record it. It is composed of a pre-positioned amplifier, a single-channel wave height analyzer, a scaler, a timer, and a counting rate meter. The functions of each part are as follows:

a) The pre-positioned amplifier transforms the pulse output impedance from the detector AND amplifies it to a certain amplitude;

b) The wave height analyzer linearly amplifies and identifies the amplitude of the output pulse of the preamplifier; it has the function of energy identification;

c) The scaler counts the pulses and shall have a counting speed and capacity that meet the counting requirements;

d) The timer is used to select the measurement time AND shall have good timing accuracy;

e) The counting rate meter is used for recording (displaying) and detecting X-ray intensity.

5.1.8 Data processing system

The computer and its software are used to correct the X-ray intensity AND convert it into the content of the analyzed elements.

5.1.9 Ventilation mechanism

In order to reduce the absorption of long-wave X-rays by the atmosphere, there shall be a vacuum system or a helium replacement system, as well as a device to maintain its pressure stably.

5.1.10 Cooling device

In order to keep the X-ray tube and high-voltage power supply in a good heat dissipation

6 Reagents and materials

6.1 Lithium tetraborate ($Li_2B_4O_7$): Before use, ignite at 600 °C for 4 hours; cool and seal for later use; it is superior grade or analytical grade.

6.2 Lithium metaborate ($LiBO_2$): before use, ignite at 600 °C for 4 hours; cool and seal for later use; it is superior grade or analytical grade.

6.3 Lithium carbonate and boron oxide (Li_2CO_3 and B_2O_3): It can replace lithium tetraborate; it is superior grade or analytical grade.

6.4 Lithium nitrate ($LiNO_3$): Superior grade or analytical grade.

6.5 Ammonium nitrate (NH_4NO_3): Superior grade or analytical grade.

6.6 Lithium bromide (LiBr): Superior grade or analytical grade.

6.7 Ammonium iodide (NH_4I): Superior grade or analytical grade.

6.8 Oxides or salts (depending on the analysis task): Spectrally pure or superior grade.

6.9 Inorganic acid: Analytically grade.

6.10 Plastic ring: Made of polyvinyl chloride material; used to strengthen the powder briquette sample during the sample preparation process of the powder briquette method.

6.11 Metal ring: Its function is the same as that of plastic ring.

7 Preparation method of sample

7.1 Solid sample preparation method

For bulk samples such as metal, alloy, cast iron, ore, glass, etc., if a suitable standard sample can be found, the bulk sample can be put into the instrument for measurement, as long as it is cut and surface polished. For other parts, such as silk, rod, sheet and other small samples of various materials, it can be crushed, melted or converted into a solution.

7.2 Powder briquette method

Weigh an appropriate amount of powdery sample, which has a particle size of less than 75 μm. Add a certain amount of diluent, grinding aid or binder as needed. Grind and mix well in the sample mill. Transfer to the tablet compression mold. Press tablets under the set tableting conditions.

The optional molds for tablet compression include: cylindrical compression mold, special sample cup, compression ring, etc. The compression ring is divided into plastic ring, metal ring, boric acid trim, etc., among which the compression ring is the most common application. The formed tablet shall have regular appearance, uniform surface, and is free from scratches or cracks.

7.3 Vitreous fusion method

In the gold platinum crucible, quantitatively weigh the analysis sample, the main flux, the flux aid, the oxidizing agent and the release agent, which has a suitable particle size, in a certain proportion. After mixing evenly, put the crucible into melting machine or muffle furnace, which was preheated to 1000 °C ~ 1200 °C for melting. After melting, transfer to the preheated gold platinum mold, to cool and solidify. The vitreous body melts in a short time and automatically peels off from the mold. The surface of the melting sheet, that is in contact with the bottom of the mold, is the measurement surface that is put into the instrument.

The formed glass sheet shall have regular appearance, smooth surface, uniform overall and no bubbles.

7.4 Solution sample preparation method

Carry out chemical treatment of a solid sample, to convert it into a solution. The standard solution and the analytical sample solution shall be similar in terms of composition and pH. The solution can be put directly into the liquid sample box for measurement, OR it can be added dropwise on filter paper or film, fixed on the support, placed in the instrument for measurement after drying.

7.5 Thin film sample preparation method

For powder samples, which have a particle size of less than 48 μm, it can be sprayed on the tape; OR sprayed on the supporting material such as filter paper by spraying technology; OR the powder sample can be mixed with an organic reagent to form a jelly, then coated on the supporting material; OR the powder sample is made into a solution, which is added dropwise on the supporting material. These methods can be made into thin film specimen. The advantage is that the spectral line intensity is not affected by the absorption enhancement effect during the measurement process.

8 Qualitative analysis

According to the analysis requirements, first determine the measurement conditions (X-ray tube current and voltage, analyzing crystal, angle scanning range, etc.). Then scan the specimen. Record the scanning process with a recorder. Then obtain a spectral line intensity and angle 2θ scanning picture. According to the angle 2θ value at the peak of the spectral line, the elements contained in the specimen can be found out, from the X-ray spectrometry (wavelength table or spectral line-2θ). Then estimate the main,

10.1.3 Powdered sample

Powders, granules, lumpy samples with uneven composition can be ground to a certain particle size by a pulverizer, grinder, etc. An appropriate amount can be directly compressed into tablets. If necessary, diluents can be added to mix OR adhesives can be pressed to form sample which has a smooth surface. Borate can also be used as a flux to melt the specimen, to cast into a glass-like frit with good uniformity, or crush the frit to form it under pressure then.

10.1.4 Liquid samples

When measuring liquid samples, the test solution shall be quantitatively divided into liquid cups. During the measurement, care shall be taken to avoid volatilization, leakage, generation of bubbles or precipitation of the test solution. It is also possible to add liquid samples dropwise to an appropriate carrier (such as filter paper) and dry them for measurement.

10.1.5 Contamination of samples

Contaminated samples will cause analytical errors. In X-ray fluorescence spectroscopic analysis, special attention shall be paid to the contamination of the sample surface. The contamination that shall be paid attention to, during the sample preparation process, has the following aspects:

a) Contamination from the material of the pulverizer and grinder;

b) Contamination from containers during dissolution and melting;

c) Contamination of the laboratory working environment;

d) Contamination of reagents;

e) Contamination caused by touching the surface of the sample with hands;

f) Contamination of lining materials;

g) Contamination caused by press molding of powder samples.

10.2 Quantitative analysis methods

10.2.1 Standard curve method

Measure a set (generally not less than 5) of standard samples, which are similar to the analytical sample (including the range of analytical element content, matrix composition, particle size, bulk density, etc.). Draw a calibration curve, for the relationship between the content of analytical elements in the standard sample with the X-ray intensity. Fit the measured intensity of the unknown sample on the standard curve, to obtain the content of the analytical elements in the unknown sample. If the linearity of the standard curve is poor, the accuracy of the determination can be improved by increasing the number of standard samples. When applying this method, attention shall be paid to the influence of coexisting elements. If necessary, an appropriate mathematical model shall be used, to obtain the influence coefficient and correct it.

10.2.2 Internal standard method

For samples that are easy to mix evenly after adding a certain component, such as a solution, the internal standard method can be used. That is to add a certain amount of internal standard elements to the sample, whose content of analytical elements is known as a standard sample; measure the X-ray intensity ratio -- of the analytical element TO the internal standard element in the standard sample; use the intensity ratio to plot the calibration curve of content of the analytical element. The same internal standard substance and the same amount are also added to the analyzed sample. The X-ray intensity ratio is obtained by the same method. The content is obtained from the calibration curve. The internal standard method is suitable for the measurement of elements, whose content is less than 10%. Care shall be taken not to cause selective absorption, selective excitation or overlapping interference to the analytical line, due to the addition of internal standard elements. Appropriate matrix element spectral lines and scattered lines can also be used as internal standard lines. It shall be noted that the internal standard elements added to each specimen are constant rather than variable.

10.2.3 Standard addition method

The standard addition method is also called the incremental method, that is, a certain amount of analytical elements are added to the sample; the content of the analytical elements in the sample is obtained, according to the change of the X-ray intensity. Using this method requires that the analysis element content has a linear relationship with the corresponding X-ray intensity, meanwhile the incremental value shall not be less than 2. This method is suitable for the determination of element content less than 10%. The standard addition method can only overcome the adverse effects, which are brought by the matrix effect under certain circumstances.

10.2.4 External standard method

Manually make a set of standard specimens, so that the basic composition of the standard sample is consistent or similar to that of the specimen to be tested; then use chemical analysis to determine the content of the analyzed elements, to make a working curve for the relationship between analytical line intensity and content. Based on the line intensity of the sample to be tested will be measured, check the element content from the working curve.

10.2.5 Mathematical methods

Mathematical methods are methods of direct mathematical calculations. It can be divided into empirical coefficient method and basic parameter method.

according to GB/T 6379.2 (repeatability, reproducibility or allowable difference). The allowable difference of the standard quantitative analysis method must meet the requirements of the technical standards for metallurgical products.

11 Common analysis software

The analysis software shall have the following functions: it can calculate the ideal α coefficient, which can reduce the number of standard samples used for calibration; it can use semi-quantitative and quantitative analysis software without standard samples; it can use more than 100 spectral lines to analyze and determine 78 elements (including Be, B, C, N, O, La, Ce, Pr, Nd and other rare earth elements) and their oxides; it can analyze solid and liquid specimen, small specimen, specimen of special shapes, as well as the calculation of thin film layers on the substrate; the specimen does not need special treatment; it can be used to analyze unknown specimens (including elements, oxides, molten samples).

12 Safety precautions

12.1 Protect against radiation from X-ray tubes. During the measurement of the instrument, it shall stop the measurement first. Then open the door of the sample chamber. It shall also regularly check the shutter device -- between the X-ray tube and the sample chamber -- for failure.

12.2 Prevent electric shock from X-ray high voltage generator. The grounding resistance of the instrument shall be less than 10 Ω. It is also necessary to regularly check whether the main contact points in the instrument are loose or rusty.

13 Recording and presentation of measurement results

13.1 Qualitative analysis results

Each detected element in the sample is represented by major amount, minor amount, trace amount, AND listed in the analysis report respectively; meanwhile the X-ray spectral line intensity and angle 2θ scanning diagram are attached.

13.2 Quantitative and semi-quantitative analysis results

When the analyzed specimen is solid, the analysis result is expressed in mass fraction (w); its unit is μg/g, mg/g, etc., or expressed in %.

When the analyzed specimen is liquid, the analysis result is expressed in mass concentration (ρ); its unit is mg/L, g/L, etc.

13.3 Measurement result record

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