Research on the method of quickly comparing the quality of titanium powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometer (EDXRF)

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Abstract: This study discloses a method for quickly comparing the quality of titanium powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometer (EDXRF), including the following steps: preparation of samples, establishment of detection methods, determination of the characteristic line fluorescence intensity values of Ti element in samples , and according to the measured fluorescence intensity values, the titanium content in the two titanium powder samples can be directly compared and determined. The method of the study has the advantages that: (1) the method is simple to operate, and the method can be repeatedly called for testing. Only one new test method needs to be built before the sample test. After the method is established, the test can be repeated at different times without re-establishing the test method for each test. After the first establishment of the new test method, the entire test process only includes three steps: sample preparation, sample loading into the sample cup and on-board testing. (2) The detection period is extremely short. After the sample is prepared, the entire measurement process takes only about 2 minutes. (3) Labor intensity is very low and the requirements for operators are not high. (4) The method has good stability, good repeatability and high credibility.

1. Introduction

The quality of titanium powder used in fireworks and firecrackers is judged by the content of titanium in titanium powder. Mentioned in the national standard “titanium powder for fireworks and firecrackers” (GB/T 20211-2006), the titanium powder for fireworks and firecrackers is divided into 1, 2, 3, and 4 grades according to the Ti titanium content. The higher the content, the higher the grade is. Taking metal titanium powder as an example, the titanium content of the grade 1 metal titanium powder is ≥90%, the titanium content of the grade 2 metal titanium powder is ≥80%, the titanium content of the grade 3 metal titanium powder is ≥70%, and the titanium of the grade 4 metal titanium powder Content ≥60%.

In the prior art, no method for quickly determining the titanium content of titanium powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy has been found, and only the method for determining titanium content in pyrotechnics for fireworks and firecrackers has been found in the National standard of “Determination of key indicators of titanium powder for fireworks and firecrackers” (GB/T 22781-2008) , and this method is based on traditional chemical analysis to quantitatively analyze the titanium content in the sample. The basic principle of this standard method: After the sample is properly pretreated, it is fully dissolved with dilute nitric acid, filtered, and then the titanium powder in the filter residue is dissolved with hydrochloric acid and filtered. After all the titanium ions are oxidized to tetravalent titanium ions with potassium chlorate, the xylenol orange is used as an indicator liquid under the condition of pH 6.0, and the titration test solution (excess EDTA) is titrated from yellow to orange with a zinc chloride standard titration solution.

The method described in this standard has the following deficiencies: (1) The detection period is long. It will takes a skilled technician two working days to complete a test. In addition, it is easy to introduce uncertainty due to insufficient proficiency of the tester during the specific test process. (2)

The operation steps are cumbersome. The sample is washed several times with absolute ethanol and acetone, then dissolved in dilute nitric acid, filtered, transferred, and collected. Then the hydrochloric acid is fully dissolved with hydrochloric acid, and then subjected to filtration, washing, and oxidation with a potassium chlorate solution. After the titanium ion is fixed to a certain volume, a certain sample solution is added to the excess EDTA, and excess EDTA is back-titrated with ZnCl2 to calculate the amount of titanium. (3) The method requires high requirements for the tester. Many steps in the operation steps are easy to introduce uncertainties such as washing, transfer, dissolution, filtration, sedimentation, enrichment, titration, etc. Each tester must be extra careful and meticulous. Otherwise, it is very easy to introduce artificial uncertainty. So far, there has not been a public literature report on the method of quickly comparing the quality of titanium powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy.

2. Theory

According to the national standards, the quality of titanium powder used for fireworks and firecrackers is judged by the content of titanium in titanium powder. After the sample is excited by X-rays, different elements in the sample emit different characteristic lines, which are fingerprint information of identifying the target elements in the sample. According to the characteristics of the chemical composition of titanium powder used for fireworks and firecrackers, a special mathematical model is established. Optimize the various factors which directly affect the results of the measurement, including: the type of method used to establish the analytical method and the voltage of the energy dispersive X-ray fluorescence spectrometer, the current, filter, peak spectrum observation line selection, analysis time, count rate, gas environment, energy range and the thickness of the sample in the sample cup and ect. Based on the assumption that the content of titanium in the powder sample is positively correlated with the fluorescence intensity of the titanium characteristic line and the ratio of the content of the titanium element to the fluorescence intensity of the characteristic line of the titanium element is a fluctuation within a certain range, it can conclude that the titanium content in the sample can be calculated semi-quantitatively by detecting the fluorescence intensity of the characteristic line of the titanium element in the sample.

3. Experiment section

3.1 Instrument and apparatus

Oven with accuracy to ±2℃. Analytical balance with accuracy to 0.1 mg. energy dispersive X-ray fluorescence spectrometer (EDXRF): United States Thermo Fisher (former Thermo Electron Corporation) Company QUANT‘X series.

3.2 Operation step

(1)10 to 30 g of the 40-100 mesh sieve sample powder is thoroughly mixed, placed in an oven, dried, placed in a desiccator and cooled to room temperature, and ready to be used.

(2) Weigh the sample of about 2 g, make sure the thickness of the powder sample in the sample cup is ≥3mm.

(3)Gently tamper the sample cup 3 times on the hard ground and put the cup in the testing tank.

(4) Set the parameters of the EDXRF instrument as shown in Table 1.

(5)Sample determination: determine the fluorescence intensity of the target element of the sample under the best analysis condition and read the values of it.

Table 1 Parameters of the EDXRF instrument

Filter	Al
Collimator	8.8mm
Voltage	20v
Electric current	Auto
Analysis time	30s
Count rate	Medium
Atmosphere	Air
Matrix effects	Not considered
Energy range	0~40kev
Analysis technique	Intensity correction
sample thickness	≥3mm

4. Results and Discussion

4.1 Sample size and particle size

In the method, 10 to 30 g of the 40-100 mesh sieve sample powder is thoroughly mixed, placed in an oven, dried, placed in a desiccator and cooled to room temperature, and ready to be used. The reason why the particle size of the sample is set to 10 ~ 30g is that in the actual production process, the quality of the titanium powder for fireworks and firecrackers is uneven and the density of the titanium powder is high, if the sample size is too small, the sample would not be representative and would be difficult to meet the requirements of the sample thickness in the sample cup which is required over 3mm thickness, and it will directly affect the accuracy of the test results. If the sample size is too large, it will affect the efficiency of the sample preparation.

There are two main reasons why the sample must be passed through a 40-100 mesh sieve: Firstly, The energy dispersive X-ray fluorescence spectrometer analyzes the surface of the sample to get the fluorescence intensity of the characteristic line of titanium element, if the sample with uneven particle size is likely to have a large particle size effect which would seriously affect the accuracy of the test results. So it must be sure to make the particle size of the sieved sample not to be too big to avoid increasing unevenness of particle size of the sample. A large amount of experimental data indicates that the particle size of the sieved sample is less than 40 mesh would cause little particle size effects. Secondly, if the titanium powder sample passes through a sieve of more than 100 meshes, the particle size will become very small, and which will not only affect the screening efficiency of the sample but also increase the dust concentration in the environment due to the too small titanium powder particles after the screening. It is also a certain health hazard to the sample preparation personnel. Another important reason is that the titanium powder with a particle size of less than 100 meshes have flammability and is easily ignited in the air.

4.2 Judgment rules

If the fluorescence intensities measured by the two samples differ by less than 5%, then the two sample masses can be considered to belong to the same level. The basis of the judgment is: 1. Due to the increase of the concentration of titanium, different elements in the sample would have a significant matrix effects on the target element, and the direct matrix effects will increase the corresponding fluorescence intensity of the characteristic line, and the influence will be random in some degree, sometimes there will be a negative growth phenomenon of the fluorescence intensity of the target element, but the impact is generally within ±2%;2. Because the sample particles of titanium powder cannot reach the ideal state of the same specification, the particle size effect is inherently present. In the process of detection by X-ray fluorescence spectroscopy, the matrix effects between elements are unavoidable, and the degree of influence of the particle size effects on the test result is generally around ±0.5%;3. Because the sample of titanium powder itself has certain non-uniformity and may contain different impurity components, the influence of the unevenness of the sample on the test results is generally about ±0.5%.In summary, According to the maximum uncertainty may be around ±4%, the method sets the uncertainty of the fluorescence intensity value of 5% to determine the quality of the two samples is based on the full consideration of the X-ray fluorescence intensity values of the different titanium powder samples in the determination process.

4.3 Advantages

The method is based on the energy dispersive X-ray fluorescence spectroscopy technology for quickly comparing the quality of titanium powder for fireworks and firecrackers, and the advantages thereof are as follows: (1) The method is simple to operate, and the method can be repeatedly called for testing. Only one new test method needs to be built before the sample test, and after the method is established, the test can be repeated at different times without re-establishing the test method for each test. After the establishment of the new test method, the entire test process only includes three steps: sample preparation, sample loading into the sample cup and on-board testing. (2) The detection period of the method is extremely short, and after the preparation of the sample, the entire measurement process only takes about 2 minutes. (3) The method has low labor intensity and is not demanding to the operator. (4) The accuracy is good, the precision is high, and the false positive rate is low.

5. Method validation test

Because the standard of pyrotechnics with a certain amount of titanium content can not be found in the market, and the physical form of black powder is similar to that of pyrotechnics, the reference material for the different titanium content of black powder as the matrix configured with the standard material of titanium powder can be tested as the samples. By comparing the correspondence between the titanium content of different pyrotechnic reference materials and their corresponding characteristic fluorescence intensity values, the general correspondence between the titanium content in the pyrotechnic composition and its corresponding characteristic fluorescence intensity would be inferred. The numerical relationship between the fluorescence intensity value and the content value of the titanium element in the samples can be seen in Table 2.

Table 2 The numerical relationship between the fluorescence intensity value and the content value of the titanium element

Sample No.	1	2	3	4	5	6
Ti content(%)	0	10	30	50	80	99.9
Ti Fluorescence intensity values(cps/mA)	0	42621	123121	193561	35473	405803
Ratio	0	4262.1	4104.0	3871.2	443.4	4062.1

It can be seen from Table 2 that: Firstly, When the sample does not contain titanium, the fluorescence intensity value of the characteristic line of the titanium element in the corresponding method is also zero. Secondly, Observing the point where the titanium content differs greatly, the fluorescence intensity value of the corresponding characteristic line is enhanced with the increase of titanium content, which is positively correlated, but not strictly proportional. The main reason is that the matrix effects of each element in the sample on the titanium element is more obvious due to the increase of the content of titanium, and the direct effects of these matrix effects will increase the corresponding difference in the fluorescence intensity value of the characteristic line of the titanium element. Thirdly, the mass percentage (%) of titanium in the sample is positively correlated with the ratio of the corresponding titanium element characteristic line fluorescence intensity value (cps/mA), and the ratio is within a range of 1:4000±10% (specific value 1:3871~4262).

6. Conclusion

This method discloses a method for quickly comparing the quality of titanium powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometer (EDXRF). Combined with the characteristics of the current titanium powder on the market, after the characteristic line fluorescence intensity values of Ti element in the sample is semi-quantitatively determined, it can accurately identify the better one from different kinds of titanium powder by comparing the fluorescence intensity values of the characteristic line of the titanium element. The method has the advantages of simple operation, short detection period, good stability, good repeatability and high credibility.

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