Research on the method of quickly comparing the quality of Aluminium 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 aluminum 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 Al element in samples, and according to the measured fluorescence intensity values, the aluminum content in the two aluminum 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 aluminum powder used in fireworks and firecrackers is judged by the content of aluminum in aluminum powder. According to the national standard "Aluminum powder for fireworks and firecrackers" (GB/T 20210-2006), the aluminum powder for fireworks and firecrackers is divided into atomized aluminum powder and ball-milled aluminum powder. The atomized aluminum powder is divided into superior products, the first-class products, the second-class products and the qualified products according to Al content. The higher class product would be with higher Al content in it. Taking atomized aluminum powder as an example, the aluminum content of superior products is ≥90%, the aluminum content of first-class products is ≥85%, the aluminum content of second-class products is ≥80%, and the aluminum content of qualified products is ≥75%.

In the prior art, no method for quickly determining the aluminum content of aluminum powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy has been found, and only the method for determining aluminum content in pyrotechnics for fireworks and firecrackers has been found in the National standard of "Determination of aluminum content in fireworks and pyrotechnics" (GB/T 20615-2006) and determination method of active aluminum content in aluminum powder in the National standard of "Chemical analysis method of Aluminium powder ,gas volume method for the determination of active aluminum" (GB 3169.1-1982), such methods are both based on traditional chemical analysis to quantitatively analyze the aluminum content in the sample. Taking the
method of "Measurement of aluminum content in pyrotechnics for fireworks and firecrackers" (GB/T 20615-2006) as an example, the basic principle of this standard method: After proper pretreatment, the sample is firstly dissolved with dilute nitric acid and filtered, and then the aluminum powder in the filter residue is dissolved with sulfuric acid, and filtered, and then the filtrate is collected, the pH of the filtrate is adjusted to some value, and the aluminum ion in the test solution is separated by adding a precipitant. EDTA complexometric titration method is to be used, and the solution condition is pH10.0 with PAN as the indicator solution. One sample solution is added with appropriate amount of ammonium fluoride to mask the aluminum ions in the test solution, and the other test solution is directly added with EDTA, and then uses copper sulfate as standard titration solution to titrate the sample solution from yellow to blue as the end point, and it can calculate the aluminum content of the sample according to the volume difference of the copper sulfate standard titration solution consumed by the two sample solutions.

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. After being dissolved in dilute nitric acid, it is filtered, transferred, and collected. Then the sulfuric acid is used to fully dissolve the filter residue, and then subjected to filtration, washing and pH adjustment. The precipitant is used to separate the aluminum ions, and finally the amount of aluminum in the solution is determined by a differential method. (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 aluminum powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy.

2. Theory
According to the national standards, the quality of aluminum powder used for fireworks and firecrackers is judged by the content of aluminum in aluminum 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 aluminum powder used for fireworks and firecrackers, a special mathematical model is established. We can 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 aluminum in the powder sample is positively correlated with the fluorescence intensity of the aluminum characteristic line and the ratio of the content of the aluminum element to the fluorescence intensity of the characteristic line of the aluminum element is a fluctuation within a certain range, it can conclude that the aluminum content in the sample can be calculated semi-quantitatively by detecting the fluorescence intensity of the characteristic line of the aluminum element in the sample.

3. Experiment section
3.1 Instrument and apparatus
Oven with accuracy to ±2°C. 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.

Table 1 Parameters of the EDXRF instrument

| Filter     | No filter |
|------------|-----------|
| 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) Sample determination: determine the fluorescence intensity of the target element of the sample under the best analysis condition and read the values of it.

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 aluminum powder for fireworks and firecrackers is uneven and the density of the aluminum 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 aluminum 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 aluminum powder sample passes through a sieve of more than 100 mesh, 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 aluminum powder particles after the screening. It is also a certain health hazard to the sample preparation personnel. Another important reason is that the aluminum powder with a particle size of less than 100 mesh has 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 aluminum, 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 aluminum 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 aluminum 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 aluminum 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 aluminum powder for fireworks and fire crackers, 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.

4.4 Method validation test
Because the standard of pyrotechnics with a certain amount of aluminum 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 aluminum content of black powder as the matrix configured with the standard material of aluminum powder can be tested as the samples. By comparing the correspondence between the aluminum content of different pyrotechnic reference materials and their corresponding characteristic fluorescence intensity values, the general correspondence between the aluminum 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 aluminum element in the samples can be seen in Table 2.

| Sample No. | 1   | 2   | 3   | 4   | 5   | 6   |
|-----------|-----|-----|-----|-----|-----|-----|
| Al content (%) | 0   | 10  | 30  | 50  | 80  | 99.9|
| Al Fluorescence intensity values (cps/MA) | 0   | 578 | 1725| 2941| 4925| 6040|
| Ratio     | 0   | 57.8| 57.5| 58.8| 61.6| 60.5|

It can be seen from Table 2 that: Firstly, When the sample does not contain aluminum, the fluorescence intensity value of the characteristic line of the aluminum element in the corresponding method is also zero. Secondly, Observing the point where the aluminum content differs greatly, the fluorescence intensity value of the corresponding characteristic line is enhanced with the increase of
aluminum 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 aluminum element is more obvious due to the increase of the content of aluminum, and the direct effects of these matrix effects will increase the corresponding difference in the fluorescence intensity value of the characteristic line of the aluminum element. Thirdly, The mass percentage (%) of aluminum in the sample is positively correlated with the ratio of the corresponding aluminum element characteristic line fluorescence intensity value (cps/mA), and the ratio is within a range of 1:60±10% (specific value 1:57.5 ~ 61.6).

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

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