# Research on rapid qualitative detection of zirconium in pyrotechnic powder used for fireworks and firecrackers

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**Abstract:** This study discloses a method for quickly qualitatively detecting the zirconium element for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometer (EDXRF), including the following steps: preparation of samples, establishment of detection methods, and determination of the characteristic line fluorescence intensity values of Sb element in samples. 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

According to the literature report, the qualitative detection method of zirconium sulfide in pyrotechnics for fireworks and firecrackers is based on traditional chemical analysis methods, and the currently used method standard is “Rules for the inspection of export fireworks and firecracker-Part 4:Safety performance test” (SN/T 0306.4-2006) ).Such standard methods have many disadvantages such as cumbersome operation steps, low detection efficiency, high use of reagents, large environmental pollution, and large influence of human factors such as judging the endpoints of coloring reaction determination.

The methods currently developed by energy dispersive X-ray fluorescence spectrometers (EDXRF) are mostly used for nondestructive qualitative analysis of samples. For semi-quantitative and quantitative elemental detection of solid samples, most samples are directly determined by powder Tableting and melting. Because pyrotechnics for fireworks and firecrackers are flammable and explosive, it is impossible to use the powder Tableting method and the melting method for sample processing. So far, there has not been a publicly reported on a method for rapidly and qualitatively detecting zirconium element in pyrotechnics for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy.

## 2. Theory

As we know, the fluorescence intensity of zirconium element of the sample powder depends on the content of zirconium in zirconium powder based on energy dispersive X-ray fluorescence spectroscopy. 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

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sample. According to the characteristics of the chemical composition of zirconium 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 zirconium in the powder sample is positively correlated with the fluorescence intensity of the zirconium characteristic line and the ratio of the content of the zirconium element to the fluorescence intensity of the characteristic line of the zirconium element is a fluctuation within a certain range, it can conclude that the zirconium content in the sample can be detected qualitatively by detecting the fluorescence intensity of the characteristic line of the zirconium 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)5 to 10 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 1 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 | Thick Pd |
| Collimator | 8.8mm |
| Voltage | 25v |
| 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 |

(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.

## 4. Results and Discussion

### 4.1 Sample size and particle size

In the method, 5 to 10 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 5 ~ 10g is that in the actual production process, the quality of the zirconium powder for fireworks and firecrackers is uneven and the density of the zirconium 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 zirconium 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 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 powder particles after the screening. It is also a certain health hazard to the sample preparation personnel. Another important reason is that the pyrotechnic sample powder with a particle size of less than 100 mesh has flammability and is easily ignited in the air.

### 4.2 Judgment rules

Different countries have different regulations on the use of prohibited substances in fireworks and firecrackers. For example, the relevant standards in the American Pyrotechnics Association stipulate that substances within 0.25% by mass of pyrotechnics are recognized as impurities. China's national standard “Safety and Quality of Fireworks and Firecracker” (GB 10631-2013) stipulates that the substance within the concentration of 0.1% by mass of pyrotechnics is recognized as an impurity, and the Netherlands found that the lead content of a certain kind of fireworks from China exceeds 120mg/kg in the results of an imported fireworks sampling test and Announced it. In combination with the actual situation of pyrotechnics for fireworks and firecrackers in China and the characteristics of energy dispersive X-ray fluorescence spectrometers, in order to effectively solve the practical problems of qualitative detection of heavy metals in fireworks and firecrackers, this method is based on the relevant content of National Standard (GB 10631-2013) to define the effective detection limitation of zirconium element is 1000 mg/kg( 0.1% by mass).

### 4.3 Advantages

The method is based on the energy dispersive X-ray fluorescence spectroscopy technology for quickly qualitatively detecting the zirconium element 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 zirconium 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 zirconium content of black powder as the matrix configured with the standard material of zirconium powder can be tested as the samples. By comparing the correspondence between the zirconium content of different pyrotechnic reference materials and their corresponding characteristic fluorescence intensity values, the general correspondence between the zirconium 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 zirconium 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 zirconium element

| Sb content (mg/kg) | 0 | 200 | 400 | 600 | 800 | 1000 | 1200 | 1400 | 1600 |
|---|---|---|---|---|---|---|---|---|---|
| Sb Fluorescence intensity values(cps/mA) | 8 | 45 | 95 | 141 | 195 | 240 | 302 | 308 | 381 |
| Sb content(%) | 1 | 10 | 50 | 80 | 99.9 | | | | |
| Sb Fluorescence intensity values(cps/mA) | 2345 | 24105 | 119586 | 19368 | 239510 | | | | |

It can be seen from Table 2 that: When the content of zirconium carbonate is in the range of 0 to 99.9%, the fluorescence intensity value of the characteristic line of zirconium element increases with the increase of zirconium carbonate content, which is positively correlated. And when the content of zirconium carbonate is in the range of 0 to 1200 mg/kg, it is substantially proportional. In particular, when the content of zirconium carbonate is 1400 mg/kg, the fluorescence intensity value of the zirconium element characteristic line (308 cps/mA) is only 6 cps/mA higher than the fluorescence intensity value at 1200 mg/kg content (302 cps/mA). Obviously, the increase of the fluorescence intensity value is not proportional to the zirconium carbonate content. The main reason is that with the increase of zirconium carbonate content in the sample, each element in the sample has an increasingly obvious matrix effects on the zirconium element and this matrix effects will increase the fluorescence intensity value of the zirconium element characteristic line randomly , sometimes the increasing amount will reduce or even be negative growth. However, when the content of zirconium compound is ≥0.1%, the fluorescence intensity value of the characteristic line of the zirconium element is always ≥240 cps/mA. Therefore, when the content of zirconium compound is in the range of 0 to 99.9%, it can be used as the basis for detecting whether the sample contains the zirconium element content above 0.1% or not that the fluorescence intensity value of the characteristic line of zirconium element is above 240 cps/mA.

## 6. Conclusion

This method discloses a method for quickly qualitatively detecting the zirconium element for fireworks and firecrackers based on EDXRF with high accuracy, good repeatability, simple operation and high efficiency. It can effectively meet the rapid detection of zirconium in pyrotechnic samples by manufacturers, regulatory authorities and third-party laboratories.

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