Research on the method of quickly identifying the types of firecracker based on energy dispersive X-ray fluorescence spectrometer (EDXRF)

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Abstract. This study discloses a method for rapidly identifying types of firecracker 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 Cl and Al elements in samples, and identification of types of firecracker based on measured fluorescence intensity values. 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
As mentioned in the Chinese national standard "Fireworks and Firecracker Safety and Quality" (GB 10631-2013), firecracker is divided into two types: black powder firecracker (BPF) and white powder firecracker (WPF). The black powder firecracker is with black powder as a blasting agent, and the white powder firecracker contains perchlorate or other oxidant and metal powder components. Due to the different types of firecracker, the national standard have different drug content limits. For example, the maximum total weight of pyrotechnic composition in a single sample of a Class C black powder firecracker cannot exceed 1g, while the maximum total weight of pyrotechnic composition in a single sample of a Class C white powder firecracker cannot exceed 0.2g. The safety production supervision administration and the quality supervision administration must firstly identify the type of firecracker in the process of firecracker production, storage and transportation, and then judge whether it is qualified according to the weight of pyrotechnic composition. At present, the commonly used methods for identifying the types of firecracker are qualitative analysis of potassium nitrate, sulfur, potassium chlorate, potassium perchlorate and aluminum or aluminum-magnesium alloy powder by conventional chemical qualitative analysis methods. The chemical qualitative analysis method has the following disadvantages: 1. Each substance required to be identified needs dozen of chemical reagents, and some are toxic and harmful. For examples, aniline hydrochloride must be used in the identification of potassium chlorate, while aniline hydrochloride is acutely toxic and is harmful to the aquatic environment and will cause irreversible damage and harm to inspectors and the environment by long-
term use. 2. The operation steps are cumbersome, the work intensity is high, and the identification efficiency is low. Each identification must separately identify 6 different substances, and each substance must be subjected to complex steps such as reagent configuration, sample preparation, sample dissolution, filtration, precipitation, and re-filtering. Usually, it takes 2 people 1~2 days to identify one sample, which greatly affects work efficiency. 3. Due to the difference of the experimental end point phenomenon and the level or the experience of the tester, there are often shortcomings such as the high false positive rate of the qualitative end point result.

2. Theory
After the sample is excited by X-rays, different elements in the sample emit different characteristic X-rays. These characteristic lines are fingerprint information of the target elements in the sample. By measuring the characteristic X-ray fluorescence intensity of the target elements in the sample, it is possible to detect whether a large amount of Cl and Al elements are present in the firecracker sample, thereby deducing the type of the firecracker sample. The method directly uses the pyrotechnic powder sample of the firecracker to establish a specific analysis method, and determines whether there are constant levels of Cl and Al elements in the sample according to the X-ray fluorescence intensity values of the Cl and Al characteristic lines. The method has the advantages of simple operation, short detection period, accurate detection result and high precision.

According to the Chinese national standard "Fireworks and Firecracker Safety and Quality" (GB 10631-2013), firecracker is divided into black powder firecracker and white powder firecracker. The key to distinguishing black powder firecracker and white powder firecracker is to identify the presence of perchlorate or other oxidants in the pyrotechnics and the metal powder components. According to the actual experience of firecracker production, the legal firecracker manufacturers that meet the safe production conditions usually use potassium perchlorate, sulfur, aluminum or aluminum-magnesium alloy powder and perlite powder for the production of firecracker. Generally, the formula of the white powder is: potassium perchlorate 40% to 60%, sulfur 10% to 30%, and aluminum or aluminum-magnesium alloy powder 10% to 30%. The formula of the black powder is about 75% potassium nitrate, 10% sulfur and 15% carbon powder. Therefore, the key to distinguishing "white powder firecracker" and "black powder firecracker" is to identify whether there is a large amount of potassium perchlorate (potassium chlorate has been banned in firecracker in the national standard) and aluminum in pyrotechnic samples. To identify whether a large amount of potassium perchlorate and aluminum are present in the sample, it is only necessary to identify whether a large amount of Cl and Al elements are present 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) Weigh the sample of about 1 g, make sure the thickness of the powder sample in the sample cup is ≥3mm.
(2) Gently tamper the sample cup 3 times on the hard ground and put the cup in the testing tank.
(3) Set the parameters of the EDXRF instrument as shown in Table 1.

| 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 Selection of the critical values

The method is based on the energy dispersive X-ray fluorescence spectroscopy technique, respectively testing the fluorescence intensity of the characteristic lines of Cl and Al elements in the pyrotechnic sample, and then based on the assumption of the fluorescence intensity values of the characteristic lines of Cl and Al elements are positively correlated with their content in the sample at a certain concentration interval, It may be inferred that the fluorescence intensity of the characteristic lines of Cl and Al elements in the sample can be used to qualitatively determine whether the sample contains a large amount of Cl and Al elements. Thereby, It can be judged whether potassium perchlorate and aluminum or aluminum-magnesium alloy powder are present in a constant content in the pyrotechnic sample. Refer to a large amount of experimental data, if the fluorescence intensity value of Cl element in the sample is $F_1 \geq 1000$ cps/mA and the fluorescence intensity value of Al element is $F_2 \geq 60$ cps/mA, it can be inferred that the sample contains potassium perchlorate and aluminum or aluminum-magnesium alloy powder in a constant content (Magnesium powder is also banned in all fireworks and firecrackers in national standards), and the result is “white powder firecracker”. If the fluorescence intensity value of the characteristic line of the Al element in the sample is $F_2 < 60$ cps/mA (normally, the fluorescence intensity value of the Al element is 0 cps/mA), it can be inferred that the sample contains no aluminum or aluminum-magnesium alloy powder (content within 1% was regarded as an impurity) and potassium perchlorate, and the result is judged as “black powder firecracker”.

In the fireworks and firecracker industry, substances with a mass percentage of less than 1% in pyrotechnics are generally considered to be impurities, which are non-human intentionally added components, and the general mass percentage of potassium perchlorate in firecracker chemicals is above 10%. It can be seen from the experimental data that the fluorescence intensity of Al element in the white powder sample with 1% aluminum content is 60 cps/mA (within ±10% deviation). And the potassium perchlorate content is 3% with the fluorescence intensity values of chlorine in the white powder samples are all 1000 cps/mA (within ±10% deviation). So, the method of the present research uses the fluorescence intensity value of 60 cps/mA as the judgment limit for the presence or absence of aluminum or aluminum-magnesium alloy powder in a constant content in the sample. The fluorescence intensity value of 1000 cps/mA is used as the judgment limit for the presence or absence of potassium perchlorate in a constant content in the sample.

4.2 Advantages

The method is based on the energy dispersive X-ray fluorescence spectroscopy technology for quickly identifying the type of 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 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.

4.3 Method validation test

In order to confirm the characteristic line fluorescence intensity values of the corresponding Cl and Al elements in different types of firecrackers, the potassium nitrate, sulfur and carbon powder were uniformly mixed in different proportions to simulate the composition of the black powder firecracker, and potassium perchlorate, sulfur, Aluminum powder and perlite powder were used to simulate the composition of the white powder firecracker. The specific test results are shown in Table 2.

| Reference substance | F1 (Cl) | F2 (Al) |
|---------------------|---------|---------|
| BPF1                | 12      | 0       |
| BPF 2               | 20      | 0       |
| BPF 3               | 23      | 0       |
| BPF 4               | 15      | 0       |
| BPF 5               | 9       | 0       |
| BPF 6               | 45      | 0       |
| WPF1                | 77673   | 2208    |
| WPF 2               | 57794   | 2055    |
| WPF 3               | 52269   | 2982    |
| WPF 4               | 63879   | 2016    |
| WPF 5               | 98773   | 1547    |
| WPF 6               | 77117   | 4251    |

From the test data in Table 5, it can be seen that the fluorescence intensity value F2 of the Al element is 0 (<60 cps/mA) in the six samples of the BPF 1 to 6, and the fluorescence intensity value F1 of the Cl element is 9 cps/mA ~45cps/mA (<1000cps/mA), and each index is in accordance with the judgement rule of “black powder firecracker” of the method. In the six samples of the WPF1 to 6, the fluorescence intensity value F2 of the Al element is 1500 cps/mA to 4300 cps/mA (≥60 cps/mA), and the fluorescence intensity value F1 of the Cl element is 52000 cps/mA to 99000 cps/mA (≥1000cps/mA), and each index is in accordance with the judgement rule of the “white powder firecracker” of the method.

5. Conclusions

This method discloses a method for quickly identifying the type of firecracker. Combined with the characteristics of the current firecracker on the market, after the characteristic line fluorescence intensity values of Cl and Al elements in the sample are qualitatively determined, it can accurately identify the type of the firecracker (black powder firecracker or white powder firecracker) by comparing the values with the preset reference values. The method has the advantages of simple operation, short detection period, good stability, good repeatability and high credibility.

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