Research on Rapid Qualitative Detection of Potassium in Pyrotechnic Powder Used for Fireworks and Firecrackers

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Abstract: This study discloses a method for quickly qualitatively detecting the potassium 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, determination of the characteristic line fluorescence intensity values of Sr 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 China National Standard “Fireworks and Firecracker-Qualitative Determination of Pyrotechnic Compositions “(GB/T 15814.1-2010) lists the relevant methods for qualitative determination of pyrotechnics in fireworks and firecrackers. The basic principle of the method: take a certain amount of sample, dissolve it with hydrochloric acid, filter it, take 1 mL of the filtrate in a test tube, and add 2 drops of sodium tetraphenylborate solution. If a white precipitate is produced, it means that there is potassium ion (when ammonium ion is present, ammonium ion should be removed).

The method described in this standard has the following deficiencies:(1) The detection time is long, and it takes half a working day for a skilled technician to complete a test. (2) The operation steps are cumbersome, and the samples are subjected to a series of steps such as dissolution, filtration, addition of indicator liquid, color reaction, etc. in order to reach a conclusion. (3) The method uses a variety of chemical reagents, and the waste liquid has a certain destructive effect on the environment. (4) The determination limit of the method is not clear, and it has little effect on the production of fireworks and firecrackers.

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 potassium elements in pyrotechnics for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy.

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2. Theory

As we know, the fluorescence intensity of potassium element of the sample powder depends on the content of potassium in potassium 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 sample. According to the characteristics of the chemical composition of potassium 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 potassium in the powder sample is positively correlated with the fluorescence intensity of the potassium characteristic line and the ratio of the content of the potassium element to the fluorescence intensity of the characteristic line of the potassium element is a fluctuation within a certain range, it can conclude that the potassium content in the sample can be detected qualitatively by detecting the fluorescence intensity of the characteristic line of the potassium 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	fiber
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

(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 potassium powder for fireworks and firecrackers is uneven and the density of the potassium 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 potassium 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.Combined with the actual situation of pyrotechnics for fireworks and firecrackers in China and the characteristics of energy dispersive X-ray fluorescence spectrometers, potassium perchlorate is commonly used raw material for pyrotechnics, and the mass percentage of potassium carbonate in pyrotechnics is generally above 10%. In order to effectively solve the practical problem of qualitative detection of commonly used raw materials in the field of fireworks and firecrackers, the method provides that the effective detection of potassium perchlorate is limited to 1%. The instrument measures the fluorescence intensity of potassium element. Since potassium perchlorate is the most commonly used in pyrotechnics, the total amount of potassium can be calculated by potassium carbonate.When the content of potassium perchlorate is 1%, the fluorescence intensity is about 640 cps/mA. In the actual production process, the mass percentage of potassium perchlorate added as a raw material is generally above 10%, and the reason why the effective detection limit of potassium element is 1% is to consider the production of fireworks and firecrackers. In fact, if the content of potassium is less than 1%, even if the detection result is “detected”, it may be an impurity mixed in the pyrotechnic composition, and it is not a raw material artificially added by the producer, So the test result has little significance for actual production guidance. If the detected content is 1% or above, the possibility of artificial addition is very large. The experimental data showed that when the content of potassium perchlorate was 1%, the fluorescence intensity value of the characteristic line of the potassium element was about 640 cps/mA (the deviation was within 10%).

4.3 Advantages

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

K content(%)	0	0.1	0.2	0.4	0.6	0.8	1	1.2	1.3
K Fluorescence intensity values(cps/mA)	0	62	125	251	367	501	640	799	812
K content(%)	1.6	1.8	2.0	10	30	50	80	99.9	
K Fluorescence intensity values(cps/mA)	1036	1129	1261	6311	19002	32368	49675	64175	

It can be seen from Table 2 that: When the content of potassium carbonate is in the range of 0 to 99.9%, the fluorescence intensity value of the characteristic line of potassium element increases with the increase of potassium carbonate content, which is positively correlated. And when the content of potassium perchlorate is in the range of 0 to 1.2%, it is substantially proportional.In particular, when the content of potassium perchlorate is 1.3%, the fluorescence intensity value of the potassium element characteristic line (812 cps/mA) is only 13 cps/mA higher than the fluorescence intensity value at 1.2% content (799 cps/mA). Obviously, the increase of the fluorescence intensity value is not proportional to the potassium perchlorate content. The main reason is that with the increase of potassium perchlorate content in the sample, each element in the sample has an increasingly obvious matrix effects on the potassium element and this matrix effects will increase the fluorescence intensity value of the potassium element characteristic line randomly , sometimes the increasing amount will reduce or even be negative growth. However, when the content of potassium perchlorate is ≥1%, the fluorescence intensity value of the characteristic line of the potassium element is always ≥640 cps/mA. Therefore, when the content of potassium element is in the range of 0 to 99.9%, it can be used as the basis for detecting whether the sample contain the potassium element content above 1% or not that the fluorescence intensity value of the characteristic line of potassium element is above 640 cps/mA.

6. Conclusion

This method discloses a method for quickly qualitatively detecting the potassium 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 potassium in pyrotechnic samples by manufacturers, regulatory authorities and third-party laboratories.

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