Research on Rapid Detection of Sulphur in Pyrotechnics

Wu Junyi[1, a], Li Yun[2], Weng Shihao[2]

[1]Beihai Customs Comprehensive Technology Service Center, Beihai, Guangxi, China

[2]Emergency Management Bureau of Pubei County, Pubei, China

[a]johnny2000@vip.qq.com

Keywords: qualitative detection; sulphur;pyrotechnic;fireworks and firecrackers.

Abstract: This study discloses a rapid qualitative detection method for sulfur in pyrotechnics for fireworks and firecrackers. It belongs to the field of analytical testing technology. Pyrotechnic samples were dissected from fireworks and firecrackers, ground, sieved, dried, cooled to room temperature, and energy dispersive X-ray fluorescence spectrometer was used as the detection instrument. The intensity method was used to establish an analytical method, and the pyrotechnic sample was loaded into the sample cup of the instrument. Then, the sample to be tested is placed in the test chamber of the test instrument, and the fluorescence intensity value of the characteristic line of the sulfur element displayed on the instrument is recorded, and the sample is directly determined whether or not the sample contains sulfur according to the fluorescence intensity value. The qualitative analysis of sulfur element is carried out by the method described in this document. It has high accuracy, good repeatability, simple operation and high efficiency. It can effectively meet the rapid detection of sulfur in the samples of pyrotechnics by manufacturers, regulatory authorities and third-party laboratories.

1. Introduction

According to the literature report, there is a method for Qualitative Detection of Sulfur in Pyrotechnics for Fireworks and Firecrackers mentioned in the China National Standard “Fireworks and Firecracker-Qualitative Determination of Pyrotechnic Compositions “ (GB/T 15814.1-2010).The basic principle of the method: the sample is dissolved with acid, 0.2 g of acid insoluble matter is taken, an appropriate amount of carbon disulfide is added, stirred, filtered, and the filtrate is collected in an evaporating dish. After the organic solvent is evaporated, the yellow residue in the evaporating dish is placed in a beaker, and dissolved by heating with 10% sodium hydroxide solution, and sodium nitrosyl iron cyanide is added a little. If the solution is purple, it means sulfur.This method has the following deficiencies: (1) The detection cycle 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 sample is subjected to a series of steps such as dissolution, filtration, stirring, re-filtration, evaporation, re-dissolution, coloring agent, color reaction, and so on. (3) The method uses a variety of chemical reagents, and the waste liquid has a certain destructive effect on the environment. (4) The detection 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 sulphur element in pyrotechnics for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy.

2. Theory

The technical problem to be solved in this document is to provide a method for rapidly and qualitatively detecting sulfur in pyrotechnics for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometry. The basic principle of detection: After the sample is excited by X-rays, different elements in the sample will emit different characteristic X-rays. These characteristic lines are fingerprint information that identifies the target elements in the sample. By determining the characteristic X-ray fluorescence intensity of the target element in the sample, it can be determined whether or not sulfur is present in the unknown sample. The method directly uses the pyrotechnic powder sample of the fireworks and firecrackers to establish a specific analysis method, and determines whether sulfur is present in the sample according to the characteristic X-ray fluorescence intensity value of the characteristic line of the sulfur element. The method has the advantages of simple operation, short detection period, good detection result accuracy and high precision.

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

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. Weigh the sample of about 1 g, make sure the thickness of the powder sample in the sample cup is ≥3mm. Gently tamper the sample cup 3 times on the hard ground and put the cup in the testing tank.Set the parameters of the EDXRF instrument as shown in Table 1. 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	No filter
Collimator	8.8mm
Voltage	6v
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 pretreatment

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 for setting the sample size of 5-10g is that the pyrotechnic powder for fireworks is a multi-component mixture explosive which is made up of many kinds of substances mechanically. If the sample size is too small, it will make the sample unrepresentative and difficult to meet the requirement that the sample thickness in the sample cup must be greater than or equal to 3mm, which will directly affect the accuracy of the test results. And Too large sample size will affect the efficiency of sample testing. Considering the complexity of pyrotechnic composition, it is very likely that the non-uniformity of samples will have a negative impact on the test results. 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 sulphur 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 Detection limit

Combined with the actual situation of pyrotechnics for fireworks and firecrackers in China and the characteristics of energy dispersive X-ray fluorescence spectrometers, sulphur powder is commonly used raw material for pyrotechnics, and the mass percentage of sulphur powder in pyrotechnics is generally above 5%. 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 sulphur is limited to 1%. The instrument measures the fluorescence intensity of sulphur element. Since sulphur powder is the most commonly used in pyrotechnics, the total amount of sulphur can be calculated by sulphur powder.When the content of sulphur powder is 1%, the fluorescence intensity is about 400 cps/mA. In the actual production process, the mass percentage of sulphur powder added as a raw material is generally above 5%, and the reason why the effective detection limitation line of sulphur element is 1% is to consider the production of fireworks and firecrackers. In fact, if the content of sulphur 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 sulphur powder was 1%, the fluorescence intensity value of the characteristic line of the sulphur element was about 400 cps/mA (the deviation was within 10%).

4.3 Method validation test

Because the standard of pyrotechnics with a certain amount of sulphur 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 sulphur content of black powder as the matrix configured with the standard material of sulphur powder can be tested as the samples. By comparing the correspondence between the sulphur content of different pyrotechnic reference materials and their corresponding characteristic fluorescence intensity values, the general correspondence between the sulphur 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 sulphur element in the samples can be seen in Table 2 and Table 3.

Table 2. The numerical relationship between the fluorescence intensity value and the content value of the sulphur element (Low concentration)

S content(%)	0	0.1	0.2	0.4	0.6	0.8	1.0	1.2	1.3	1.6	1.8	2.0
S fluorescence intensity values(cps/mA)	0	40	83	151	228	302	410	495	502	621	730	809

Table 3. The numerical relationship between the fluorescence intensity value and the content value of the sulphur element (constant concentration)

S content(%)	0	1	10	30	50	80	99.9
S luorescence intensity values(cps/mA)	0	406	3985	11458	20612	31475	41362

It can be seen from Table 2 and Table 3 that: When the content of sulphur powder is in the range of 0 to 99.9%, the fluorescence intensity value of the characteristic line of sulphur element increases with the increase of sulphur content, which is positively correlated. And when the content of sulphur is in the range of 0 to 1.2%, it is substantially proportional. In particular, when the content of sulphur powder is 1.3%, the fluorescence intensity value of the sulphur element characteristic line (502 cps/mA) is only 7 cps/mA higher than the fluorescence intensity value at 1.2% content (495 cps/mA). Obviously, the increase of the fluorescence intensity value is not proportional to the sulphur powder content. The main reason is that with the increase of sulphur powder content in the sample, each element in the sample has an increasingly obvious matrix effects on the sulphur element and this matrix effects will increase the fluorescence intensity value of the sulphur element characteristic line randomly , sometimes the increasing amount will reduce or even be negative growth.However, when the content of sulphur powder is ≥1%, the fluorescence intensity value of the characteristic line of the sulphur element is always ≥400 cps/mA. Therefore, when the content of sulphur element is in the range of 0 to 99.9%, it can be used as the basis for detecting whether the sample contain the sulphur element content above 1% or not that the fluorescence intensity value of the characteristic line of sulphur element is above 400 cps/mA.

4.4 Repeatability test of the method

The purpose of this repeatability test is to confirm the fluorescence intensity of the characteristic spectral lines of sulfur element corresponding to the mass percentage of sulfur element in different types of pyrotechnics when its content is 1%. Using different types of pyrotechnics as substrates and adding sulfur reference materials, a pyrotechnic reference material with sulfur element content of 1% is prepared for determination. The energy dispersive X-ray fluorescence spectrometer (EDXRF) is a measuring instrument to measure the fluorescence intensity of sulfur characteristic lines in pyrotechnics with the same sulfur content. The parameters of the measuring instrument are as follows: collimator aperture is 8.8 mm, no filter is set, voltage is 20 kV, analysis time is 30 s, energy range is 0-40 keV, counting rate is medium. The gas environment is air, the current is automatic and the peak spectrum observation line is K line. The specific test results are shown in Table 4.

Table 4: Fluorescence intensity values of characteristic lines of sulfur in different type of pyrotechnic samples

Sample	Sulfur content (%)	Fluorescence intensity of sulfur
Black Powder Matrix Reference Material	1	410
Red effect pyrotechnic matrix reference material	1	398
Red effect pyrotechnic matrix reference material	1	402
Red effect pyrotechnic matrix reference material	1	385
Red effect pyrotechnic matrix reference material	1	421
Red effect pyrotechnic matrix reference material	1	392
Firecracker Agent matrix reference material	1	406

According to the experimental data in Table 4, when the content of sulfur is 1%, the fluorescence intensity of the characteristic lines of sulfur is about 400 cps/mA in different pyrotechnic powder samples, and the difference is within (+10%).

5. Conclusions

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

References

[1] Leif, H. C.; Allan, A. Determination of sulfur and heavy metals in crude oil and petroleum products by energy-dispersive x-ray fluorescence spectrometry and fundamental parameter approach.Anal. Chem.,53(12),pp.1788-1792,1981.

[2] Fei, H; Pierre, J. V. E. General approach for quantitative energy dispersive x-ray fluorescence analysis based on fundamental parameters. Anal. Chem.,63(20),pp.2237-2244,1991.

[3] Standard test method for determination of lead in paint layers and similar coatings or in substrates and homogenous materials by energy dispersive x-ray fluorescence spectrometry using multiple monochromatic excitation beams,ASTMF2853,American Society for Testing and Materials Publications, 2010.

[4] Standard test method for analysis of uranium and thorium in soils by energy dispersive x-ray fluorescence spectroscopy, ASTM C1255,American Society for Testing and Materials Publications, 2011.

[5] Duan Tiyu, Li Suqing, et al. Jewellery,Determination of precious metal content - Method using x-ray fluorescence spectrometry,China National Recommended Standard: GB/T 18043-2013, China Standard Press: Beijing, 2014.

[6] Leoni. L,Saitta. M, X-ray fluorescence analysis of powder pellets utilizing a small quantity of material, X-ray Spectrom, 3,pp.74-77,1974.

[7] Rose W.I.,Bornhorst T.J.,Sivonen S.J., Rapid high-quality major and trace element analysis of powdered rock by x-ray fluorescence spectrometry, X-ray Spectrom, 15,pp.55-60,1986.

[8] Gy, Pierre M, The analytical and economic importance of correctness in sampling, Anal.Chim.Acta, 190,pp.13-23,1986.

[9] Zhou Tonghui, Wang Erkang, Lu Wanzhen ect. Handbook in analytical chemistry(second edition), basic knowledge of and safety knowledge(the first volume) , China Chemical industry press:pp.568-580,1997.