

Research on rapid semi-quantitative determination of sulfur in pyrotechnics

Wu Junyi

Technology Center for Dangerous Goods of Nanning Customs, Beihai, Guangxi, China

johnny2000@vip.qq.com

Keywords: semi-quantitative; sulfur; pyrotechnics; fireworks and firecrackers.

Abstract: This study discloses a method for rapid semi-quantitative determination of sulfur in pyrotechnic powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometer (EDXRF), including the following steps: preparation of samples, establishment of testing methods, determination of the characteristic line fluorescence intensity values of Al element in samples, and according to the measured fluorescence intensity values, the sulfur content in the pyrotechnic powder samples can be semi-quantitatively 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 testing time 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

In the prior art, no method for quickly semi-quantitatively determining the sulfur content in pyrotechnics used for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy has been found, and only the method for determining sulfur content in pyrotechnics for fireworks and firecrackers has been found in the Industry standard of "Pyrotechnics used for fireworks and firecrackers Part 10: determination of sulfur content" (SN/T 1732.10-2014), such method is based on traditional chemical analysis to quantitatively analyze the sulfur content in the sample, and 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, then dissolved in hot water, filtered, transferred, and collected, and then precipitated, enriched, filtered, dried, and weighed with sodium tetraphenylborate solution, and finally get the potassium content. (3) The method requires high requirements for the tester. Many steps in the operation steps involving washing, transfer, dissolution, filtration, precipitation, enrichment, etc., which are easy to introduce uncertainty. Each tester must be extra careful and meticulous. Otherwise, it is very easy to introduce artificial uncertainty.

The methods currently developed by energy dispersive X-ray fluorescence spectroscopy are mostly used for non-destructive qualitative analysis of samples. For semi-quantitative and quantitative elemental detection of solid samples, most samples are directly determined by powder Tableting or melting methods, such as: "Determining the content of precious metals by X-ray fluorescence spectrometry" (GB/T 18043-2008) using non-destructive Detection method, "Alumina chemical analysis method and physical property measurement method Part 30 X-ray fluorescence spectrometry determination of element content" (GB/T 6609.30-2009) using the melting method, "EDXRF method for direct determination of W-Fe- Ni-Co Alloy Mixture Components ("Nuclear Electronics and Detection Technology" Issue 5, 2007) uses the Tableting method, "X-ray

fluorescence spectrometry for rapid determination the contents of potassium, sodium, calcium and magnesium in potassium chloride products”. (Analytical Instruments, Issue 6, 2013) using the Tableting method, “Rapid screening X-ray fluorescence spectrometry for lead, mercury, chromium, cadmium and bromine in electronic and electrical products” (GB/Z 21277) -2007) uses the Tableting method or the melting method. Because pyrotechnics for fireworks and firecrackers are flammable and explosive, it is impossible to Tablet or melt the pyrotechnic powder for the sample preparation. So far, there has been no published literature report on the method of rapid semi-quantitative determination of sulfur content in pyrotechnics for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometry.

2. Theory

After the pyrotechnic sample is excited by X-rays, different elements in the sample emit different characteristic X-rays. These characteristic lines are fingerprint information that identifies the target element in the sample. By measuring the characteristic X-ray fluorescence intensity of the target element in the sample, it is possible to semi-quantitatively analyze the amount of sulfur in the unknown pyrotechnic sample. The method directly uses the pyrotechnic powder sample of the fireworks and firecrackers to establish a specific analysis method, and semi-quantitatively analyzes the sulfur content in the sample according to the X-ray fluorescence intensity value of the characteristic line of the sulfur element.

3. Experiment section

3.1 Instrument and apparatus

Oven with accuracy to $\pm 2^{\circ}\text{C}$. 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 $\geq 3\text{mm}$.
- (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	6v
Electric current	Auto
Analysis time	30s
Count rate	Medium
Atmosphere	Vacuum
Matrix effects	Not considered
Energy range	0~40kev
Analysis technique	Intensity correction
sample thickness	$\geq 3\text{mm}$

(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.

(5) Calculate the amount of sulfur in the sample by calculating the fluorescence intensity value according to the following formula:

$$\omega = \frac{F}{C}$$

Wherein, ω indicates the mass percentage of sulfur in the sample, the unit is %; C is the fluorescence intensity value of the corresponding characteristic line when the mass percentage of sulfur element in the sample is 1%, and the unit is cps/mA; F is the fluorescence intensity value of the characteristic line of the sulfur element measured by the energy dispersive X-ray fluorescence spectrometer in units of cps/mA.

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 pyrotechnic powder for fireworks and firecrackers is uneven and the density of the sulfur 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 sulfur 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 pyrotechnic 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 sulfur powder particles after the screening. It is also a certain health hazard to the sample preparation personnel. Another important reason is that the pyrotechnic powder with a particle size of less than 100 mesh has flammability and is easily ignited in the air .

4.2 Advantages

A method for rapid and semi-quantitative determination of sulfur content in pyrotechnic samples of fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometry, the advantages of which 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 analysis time of the method is extremely short, and after the preparation of the sample, the entire measurement process only takes about 1 minute. (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

Because the standard of pyrotechnics with a certain amount of sulfur 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 sulfur content of black powder as the matrix configured with the standard material of sulfur powder can be tested as the samples. By comparing the correspondence between the sulfur content of different pyrotechnic reference materials and their corresponding characteristic

fluorescence intensity values, the general correspondence between the sulfur 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 sulfur 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 sulfur element

Sample No.	1	2	3	4	5	6
S content(%)	0	10	30	50	80	99.9
S Fluorescence intensity values(cps/mA)	0	3985	11458	20612	31475	41362
Ratio	0	398.5	381.9	412.2	393.4	414.0

It can be seen from Table 2 that: Firstly, When the sample does not contain sulfur, the fluorescence intensity value of the characteristic line of the sulfur element in the corresponding method is also zero. Secondly, Observing the point where the sulfur content differs greatly, the fluorescence intensity value of the corresponding characteristic line is enhanced with the increase of sulfur 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 sulfur element is more obvious due to the increase of the content of sulfur, and the direct effects of these matrix effects will increase the corresponding difference in the fluorescence intensity value of the characteristic line of the sulfur element. Thirdly, The mass percentage (%) of sulfur in the sample is positively correlated with the ratio of the corresponding sulfur element characteristic line fluorescence intensity value (cps/mA), and the ratio is within a range of $1:400 \pm 5\%$ (specific value $1:381.9 \sim 414.0$).

4.4 Method repeatability test

The purpose of the method repeatability test is to further confirm the corresponding characteristic fluorescence intensity values of sulfur elements when sulfur has a mass percentage of 10% in different types of pyrotechnic agents. The samples of pyrotechnic reference materials with an sulfur content of 10% were determined by using different types of pyrotechnic agents as substrates. The specific test results are shown in Table 3.

Table 3. Fluorescence intensity values of characteristic lines of sulfur in different pyrotechnic reference materials with an sulfur content of 10%

Sample No.	1	2	3	4	5
Pyrotechnic effects	Red	Blue	Yellow	Green	White
S Fluorescence intensity values(cps/mA)	4120	3980	3846	4031	3886
Ratio	412	398	384.6	403.1	388.6

It can be seen from the test data of Table 3 that when the content of sulfur element in the sample of different pyrotechnic composition is 10%, the fluorescence intensity value of the corresponding sulfur element characteristic line ranges from 3846 to 4120 cps/mA. The ratio of the content of sulfur in the pyrotechnic composition to the corresponding fluorescence intensity value of the sulfur element is also positively correlated and fluctuates within a certain range (specific values are $1:384.6$ to 412). Since it is a semi-quantitative test, this proportional coefficient can be approximated by an integer multiple of $1:380$ to $1:410$.

5. Conclusions

This article discloses a method for quickly and semi-quantitatively detecting sulfur content in pyrotechnic blind samples of fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometer (EDXRF), and the method has the advantages of simple operation, short

detection period, good stability, good repeatability and high credibility.

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, ASTM F2853, 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 Tong-hui, WANG Er-kang, LU Wan-zhen et al. Handbook in analytical chemistry (second edition), basic knowledge of and safety knowledge (the first volume), China Chemical industry press: pp.568-580, 1997.