Research on rapid qualitative detection of copper in pyrotechnics

Junyi Wu[1, a], Tairong Lu[2], Rui Wu[3], Pengpeng Zhang[3]

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

[2]China Academy of Science & Technology Development Guangxi branch, Guangxi, China

[3]Guangxi zero to One Technology co. LTD, Guangxi, China

[a]johnny2000@vip.qq.com

Keywords: Qualitative detection; copper; pyrotechnic; fireworks and firecrackers.

Abstract: This study discloses a method for quickly qualitatively detecting the copper 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 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 common methods of qualitative detection in pyrotechnics for fireworks and firecrackers. However, the rapid qualitative detection method of the most commonly used copper elements in the fireworks industry is missing.

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

2. Theory

As we know, the fluorescence intensity of copper element of the sample powder depends on the content of copper oxide in pyrotechnic 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 copper oxide 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

  DOI: 10.25236/acete.2019.002

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 copper oxide in the powder sample is positively correlated with the fluorescence intensity of the copper characteristic line and the ratio of the content of the copper element to the fluorescence intensity of the characteristic line of the copper element is a fluctuation within a certain range, it can conclude that the copper content in the sample can be detected qualitatively by detecting the fluorescence intensity of the characteristic line of the copper 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	Medium thick Pd
Collimator	8.8mm
Voltage	20 v
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 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 copper oxide for fireworks and firecrackers is uneven and the density of the copper oxide 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 copper 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, copper oxide is commonly used raw material for pyrotechnics, and the mass percentage of copper oxide in pyrotechnics is generally above 3%. 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 limit of copper is 1% The instrument measures the fluorescence intensity of copper element. Since copper oxide is the most commonly used in pyrotechnics, the total amount of copper can be calculated by copper oxide.When the content of copper oxide is 1%, the fluorescence intensity is about 1150 cps/mA. In the actual production process, the mass percentage of copper oxide added as a raw material is generally above 3%, and the reason why the effective detection limit of copper element is 1% is to consider the production of fireworks and firecrackers. In fact, if the content of copper oxide 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 is1% or above, the possibility of artificial addition is very large. The experimental data showed that when the content of copper oxide was 1%, the fluorescence intensity value of the characteristic line of the copper element was about 1150 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 copper 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.

4.4 Method validation test

Because the standard of pyrotechnics with a certain amount of copper 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 copper content of black powder as the matrix configured with the standard material of copper oxide can be tested as the samples. By comparing the correspondence between the copper content of different pyrotechnic reference materials and their corresponding characteristic fluorescence intensity values, the general correspondence between the copper 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 copper 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 copper element (Low concentration)

Cu content (%)	0	0.1	0.2	0.4	0.6	0.8	1.0	1.2	1.3	1.6
Cu luorescence intensity values(cps/mA)	0	111	224	449	682	929	1153	1403	1415	1823

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

S content (%)	0	1	10	30	50	80	99.9
S luorescence intensity values(cps/mA)	0	1176	11372	33676	58123	88541	118487

It can be seen from Table 2 and Table 3 that: When the content of copper oxide is in the range of 0 to 99.9%, the fluorescence intensity value of the characteristic line of copper element increases with the increase of copper oxide content, which is positively correlated. And when the content of copper oxide is in the range of 0 to 1.2%, it is substantially proportional. In particular, when the content of copper oxide is 1.3%, the fluorescence intensity value of the copper element characteristic line (1415 cps/mA) is only 12 cps/mA higher than the fluorescence intensity value at 1.2% content (1403 cps/mA). Obviously, the increase of the fluorescence intensity value is not proportional to the copper oxide content. The main reason is that with the increase of copper oxide content in the sample, each element in the sample has an increasingly obvious matrix effects on the copper element and this matrix effects will increase the fluorescence intensity value of the copper element characteristic line randomly , sometimes the increasing amount will reduce or even be negative growth.However, when the content of copper oxide is ≥1%, the fluorescence intensity value of the characteristic line of the copper element is always ≥1150 cps/mA. Therefore, when the content of copper element is in the range of 0 to 99.9%, it can be used as the basis for detecting whether the sample contain the copper element content above 0.25% or not that the fluorescence intensity value of the characteristic line of copper element is above 1150 cps/mA.

5. Conclusions

This method discloses a method for quickly qualitatively detecting the copper 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 copper 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.