

Research on rapid semi-quantitative determination of mercury in pyrotechnics used for fireworks and firecrackers

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Abstract: This study discloses a method for rapid semi-quantitative determination of mercury 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 Hg element in samples, and according to the measured fluorescence intensity values, the mercury 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 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

In the prior art, no method for quickly determining the mercury content of mercury powder for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectroscopy has been found, and only the method for determining mercury content in other fields. Such as: Iron ores-Determination of arsenic, chromium, cadmium, lead and mercury content-inductively coupled plasma mass spectrometry (ICP-MS) (GB/T 6730.72-2016), "Chromium ores- Determination of mercury content-solid injection directly Determination method (GB/T 31948-2015) and "Inorganic chemicals for industrial use-General method for mercury content-flameless atomic absorption spectrometric method" (GB/T 21058-2007). Most of these standard methods use instruments such as inductively coupled plasma spectroscopy-mass spectrometry, atomic absorption spectrophotometer, and direct mercury analyzer, and substantially no energy dispersive X-ray fluorescence spectrometer is used.

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/T6609.30-2009) 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 mercury 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 mercury 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 mercury content in the sample according to the X-ray fluorescence intensity value of the characteristic line of the mercury 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	Thick Pd
Collimator	8.8mm
Voltage	30v
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	$\geq 3\text{mm}$

(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 mercury in the sample by calculating the fluorescence intensity value according to the following formula:

$$\omega = C \times F$$

Wherein, ω indicates the mass content of mercury in the sample, the unit is mg/kg; C indicates the corresponding mercury content of the characteristic line fluorescence intensity value of mercury

in the sample at 1 cps/mA, the unit is mg/kg; F indicates the fluorescence intensity of the characteristic line of mercury element measured by the energy dispersive X-ray fluorescence spectrometer, the unit is 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 mercury 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 mercury 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 mercury 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 mercury 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 mercury 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 mercury content of black powder as the matrix configured with the standard material of mercury powder can be tested as the samples. By comparing the correspondence between the mercury content of different pyrotechnic reference materials and their corresponding characteristic fluorescence intensity values, the general correspondence between the mercury 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 mercury 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 mercury element

Sample No.	1	2	3	4	5	6
Cd content(mg/kg)	0	1000	5000	10000	30000	50000
Cd Fluorescence intensity values(cps/mA)	0	48	262	523	1612	2632
Ratio	0	20.8	19.1	19.1	18.6	19.0

It can be seen from Table 2 that: Firstly, When the sample does not contain mercury, the fluorescence intensity value of the characteristic line of the mercury element in the corresponding method is also zero. Secondly, Observing the point where the mercury content differs greatly, the fluorescence intensity value of the corresponding characteristic line is enhanced with the increase of mercury 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 mercury element is more obvious due to the increase of the content of mercury, and the direct effects of these matrix effects will increase the corresponding difference in the fluorescence intensity value of the characteristic line of the mercury element. Thirdly, The mercury content (mg/kg) in the sample is positively correlated with the ratio of the corresponding mercury element characteristic line fluorescence intensity value (cps/mA), and the ratio is within a range of $19:1 \pm 10\%$ (specific value is 18.6~20.8:1).

4.4 Method repeatability test

The purpose of the method repeatability test is to further confirm the corresponding characteristic fluorescence intensity values of mercury elements when mercury has a mass percentage of 0.1% in different types of pyrotechnic agents. The samples of pyrotechnic reference materials with an mercury content of 0.1% 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 mercury in different pyrotechnic reference materials with an mercury content of 0.1%

Sample No.	1	2	3	4	5
Pyrotechnic effects	Red	Blue	Yellow	Green	White
Cd Fluorescence intensity values(cps/mA)	52	48	47	51	50
Ratio	19.2	20.8	21.3	19.6	20.0

It can be seen from the test data of Table 3 that when the content of mercury element in the sample of different pyrotechnic composition is 0.1% (1000 mg/kg), the fluorescence intensity value of the corresponding mercury element characteristic line ranges from 47 to 52 cps/mA. The ratio of the content of mercury in the pyrotechnic composition to the corresponding fluorescence intensity value of the mercury element is also positively correlated and fluctuates within a certain range (specific values are 1:19.2~1:21.3). Since it is a semi-quantitative test, this proportional coefficient can be approximated by an integer multiple of 1:19 to 1:21.

5. Conclusions

This article discloses a method for quickly and semi-quantitatively detecting mercury 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.

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