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Determination of iron content in pyrotechnics used for fireworks and firecrackers based on Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF）

Wu Jun-yi[1, a]

[1]Technical Center for Dangerous Goods Testing of Guangxi Entry-Exit Inspection and Quarantine Bureau, Beihai, Guangxi, China

[a]johnny-woo@vip.163.com

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Abstract. Methods used for the determination of iron content in pyrotechnics are mostly based on traditional chemical method, which is lengthy and cumbersome. If inductively coupled plasma emission spectrometry or atomic absorption spectrometry are used to determine the iron with high content, the sample solution must be highly diluted, and it must produce errors in measurement and calling into question the reliability of the data. The method mentioned in this paper is about the determination of iron content in pyrotechnics used for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometry by controlling matrix effects between elements. Using sample solution of pyrotechnics in specific concentrates, the iron content can be determined by the specific calibration curve established with an intensity calibration. This method can provide high accuracy and good precision in a short time with a simple process by efficiently controlling the matrix effects. It can fully meet the requirements for the determination of iron in pyrotechnics used for different kinds of fireworks and firecrackers around the world, and it has good generalization and practicability. The average recovery of the method can be 96.97%～99.23%, allowing for a difference of 0.5%.

Introduction

In China, fireworks and firecrackers are very important consumer recreational products in people's everyday life since ancient times. Gorgeous colors produced by fireworks and firecrackers are even the iron ing role of foiling festal atmosphere in every grand holiday celebrations. In recent years, with the rapid development of global trade, fireworks and firecrackers are becoming more and more popular all over the world, more and more consumers are fascinatedby different kinds of patterns, pictures, and sound effects of fireworks and firecrackers. Iron element is commonly found in iron powder and iron oxide as primary materials used for pyrotechnics. Quantitative analysis of chemical compositions in pyrotechnics such as iron content is required under the Globally Harmonized System of Classification and Labeling of Chemicals(GHS)to be complemented in the fireworks and firecrackers industry. Meanwhile it will also provide a scientific and effective technical support to the management and supervision of safety production for the government, and improve products' quality level by the manufacturers. It can also be utilized as a tool in providing valuable data in the judgment in some major arbitration and security incident analysis. Quantitative analysis method of the iron content reported in current literature is limited to traditional chemical analysis, such methods have the following disadvantages:(1) Long detecting period. Generally, it will take a skilled technician two whole days or so to complete the detection.(2) The operation is more complicated. It needs to go through many steps such as dissolving sample, filtration, precipitation collection, drying and weighing precipitation and ect. Comparing with traditional chemical analysis methods ,this method

based on energy dispersive X-ray fluorescence spectrometry(EDXRF) has the advantages of simple operation steps, short period of detection, high accuracy and good precision.

Theory

Iron element is commonly found as primary content in chemical materials such as iron powder and iron oxide in pyrotechnics used for fireworks and firecrackers. Statistical analysis shows that iron powder and iron oxide in pyrotechnics is between 5% to 20% ,it can concludes that the iron content in pyrotechnics would be 3%～15% as mass fraction.Concept of the method: considering the weight of the sample is 2.0 g,constant volume is 0.5 L and the concentrations of the iron would be controlled in 0.12 g/L～0.60 g/L in sample solutions. And it can prove that when the iron content in the solution is in the range of 0.08 g/L～0.66g/L, there would be little matrix effects among elements. So we can establish a working curve which contains the iron elements with the content of 0.08 g/L～0.66g/L to determine the iron content in the sample solution. In accordance with the relevant safety regulations, the sample was ground into powder of less than 180 micron. Then the sample powder is placed in an explosive–proof oven at 50℃–55℃ and dried for 4 hours, and then placed into a dryer for cooling down to room temperature. Pretreated sample is fully dissolved in pure water and nitric acid seperately and then filtered into volumetric flask as sample solution. The sample solution can be put into the sample cup and placed in the tank of the EDXRF to measure the fluorescence intensity of the iron elements. The actual content of iron element in the sample can be calculated from the concentrations of the iron reading by the working curve.

Experiment section

Reagents

Unless otherwise stated, all the reagents should be guaranteed reagents and pure water is secondary grade water as described in ISO 3696(1987). Nitric acid (1+1): mix nitric acid and pure water thoroughly according to the proportion of 1:1. Standard working solution of the iron nitrate: Weigh 0.83 g high purity iron powder reference materials (accuracy to 0.1 mg), and put it in a 300 ml beaker, add 50 mL nitric acid (1+1), heat the beaker and make the sample solution slightly boiling on an electric stove for 20 min. After the solution is cool down to the room temperature, transfer the solution into a 500 ml volumetric flask, add pure water to the scale.Then we can separately pipette the standard working solution of the nitric acid with volume 5 mL、10 mL、15 mL、20 mL、25 mL、30 mL、35 mL and 40 mL into eight 100 mL volumetric flasks which marked from N_1 to N_8, and add pure water to reach 100 mL in each volumetric flask, mix thoroughly for later use. Concentrations of the standard working solution in different flasks are shown in Table 1.

Table 1 Fluorescence intensity of series standard working solutions of irong/L

NO.	Mass concentration (g/L)	Fluorescence intensity (cps/mA)
N_1	0.0830	161.77
N_2	0.1661	312.46
N_3	0.2491	484.73
N_4	0.3321	636.13
N_5	0.4152	808.25
N_6	0.4982	933.84
N_7	0.5812	1094.45
N_8	0.6643	1205.25

Instrument and apparatus

Explosive-proof 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.

Operation step

(1) Weigh the sample of about 2.0 g, accuracy to 0.1 mg.
(2) Place the sample into a clean 300 mL beaker, add 150 mL pure water into the beaker, then place the beaker on an electric stove to make the solution boiled for about 10 min. Filter the solution through filter paper and collect the residue to another 300 mL beaker, add 80 mL nitric acid (1+1) to the beaker, then place the beaker on an electric stove to make the solution boiled for about 20 min. Filter the solution through filter paper to an 0.5 L volumetric flask, wash the beaker and the filter paper several times with pure water, and make a constant volume with pure water after the filtered solution cooling down to room temperature.
(3) Parameters of the EDXRF instrument parameters are shown in Table 2.

Table 2 Parameters of the EDXRF instrument

Filter	Thin Pd
Collimator	8.8mm
Voltage	20v
Electric current	Auto
Analysis time	50s
Count rate	Medium
Atmosphere	Air
Matrix effects	Not considered
Energy range	0～40kev
Analysis technique	Intensity correction
sample thickness	≥15mm

(4) Calibration (working) curve: according to the requirements of the method and the instrument criteria, we set the instrument to optimum analysis conditions, and adjust it to the best working condition, and determine spectral intensity of the series standard solution from N_1 to N_8 to establish the calibration (working) curve with the elemental concentrations as independent variable and the spectral intensity as the dependent variable. The linear correlation coefficient of the regression curve should be 0.99 or higher.
(5) Sample determination: determine the fluorescence intensity of the iron in blank solution and every sample solution under the best analysis condition and read the concentrations from the calibration curve according to the spectral intensity.

Results calculation

Content of the iron element in the sample can be calculated as mass fraction *W* and its value shown in% according to the following formula.

$$\omega = \omega_0 \times \frac{2.0}{\mathrm{m}} \times \frac{V}{500}$$

Where: ω_0—the content of the iron in the sample read by the working curve, expressed in %.
m—quantity of the sample, expressed in milligrams (g).
V—constant volume of the volumetric flask used for the sample solution, expressed in liters(mL).
ω— the content of the iron in the sample, expressed in %.
2.0—assume that quantity of the sample, expressed in milligrams (g).

500—assume that constant volume of the volumetric flask used for the sample solution, expressed in liters(mL).

Results and discussion

Solvent selection

Considering the characteristics of the EDXRF spectrometry, this method selects nitric acid as the solvent for the sample instead of some other strong acids such as hydrochloric acid, sulfuric acid, or perchloric acid, which are usually recommended in relevant papers. If these strong acids were to be selected as the solvents to dissolve the sample, great amounts of chlorine and sulfur elements would be introduced to the sample solution, and these would make great matrix effects on the iron element and affect the accuracy of the test. On the contrary, if nitric acid are used as the solvents, only the nitrogen elements are introduced to the sample solution. So, the other elements would have little matrix effects on the iron element and can be basically ignored.

Selection of standard solution.

Considering that all the most of the iron element come from iron powder or iron oxide in pyrotechnics used for fireworks and firecrackers. In order to make the standard solution as consistent as possible with the sample solution, the iron standard solution would be selected to make the working curve. It proved that when the concentration of the iron element is controlled to the range of 0.12 g/L～0.60 g/L, it would have little matrix effects on the iron element and can be basically ignored. Because the contents of other impurity elements such as aluminum and manganese are all mostly less than the iron element, they would also have little matrix effects on the iron element in the sample solution.

Recovery test

To assess the accuracy of the method, we used the standard reference substances addition recovery test. We added the iron powder or iron oxide reference standard substances to some actual black powder samples or some pyrotechnics without any iron, dissolved the samples and determined the contents of iron in the sample solution. The values of the iron contents we measured are compared with the theoretical ones, and the experimental data is shown in Table 3 below.

Table 3 Recovery test results

NO.	Reference materials	Reference Code	Iron content of nominal (%)	Iron content of measurment (%)	recovery rate（%）
1	Pyrotechnics	Fe01	15.6	15.3	98.08
2	Pyrotechnics	Fe02	10.9	10.6	97.25
3	Pyrotechnics	Fe03	6.6	6.4	96.97
4	Iron standard solution	Fe04	30.6	30.1	98.37
5	Iron standard solution	Fe05	25.9	25.7	99.23
6	Iron standard solution	Fe06	20.5	20.3	99.02
7	Iron standard solution	Fe07	14.5	14.3	98.62
8	Iron standard solution	Fe08	12.5	12.3	98.40
9	Iron standard solution	Fe09	8.7	8.5	97.70
10	Iron standard solution	Fe10	3.5	3.4	97.14
Average（X）					98.08
standard deviation (S)					0.75

Conclusions

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is used to determine the iron content in pyrotechnics used for fireworks and firecrackers, this method is accurate and quick with high accuracy and good precision. When the iron content in the sample is in the range of 3%～30% as mass fraction, the recovery is 96.97%～99.23%.The allowable differential value was 0.5% between two single tests under repeatable conditions. In other word, this method can completely satisfy the requirements of the fireworks and firecrackers industry.

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