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

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Abstract. Methods used for the determination of chromium 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 chromium 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 chromium 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 chromium 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 chromium 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 reach 95.26%～98.71%, 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 chromium 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. Pyrotechnics used to produce various kinds of pyrotechnic effects in fireworks and firecrackers are consists of many different solid chemicals. Chromium element is commonly found in pyrotechnics as primary content used for fireworks and firecrackers. Quantitative analysis of chemical compositions in pyrotechnics such as chromium 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 chromium 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

Chromium   element is commonly found as primary content in chemical materials such as potassium chromate and potassium dichromate in pyrotechnics used for fireworks and firecrackers. Statistical analysis shows that potassium chromate and potassium dichromate in pyrotechnics is between 10% to 30% ,it can concludes that the chromium content in pyrotechnics would be 2.6%～ 11% as mass fraction.Concept of the method: considering the weight of the sample is 1.5g,constant volume is 0.5L and the concentrations of the chromium would be controlled in 0.08g/L～0.33g/L in sample solutions. And it can prove that when the chromium content in the solution is in the range of 0.03g/L～0.58g/L, there would be little matrix effects among elements. So we can establish a working curve which contains the chromium elements with the content of 0.03g/L～0.58g/L to determine the chromium 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°C–55°C 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 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 chromium elements. The actual content of chromium element in the sample can be calculated from the concentrations of the chromium 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+4): mix nitric acid and pure water thoroughly according to the proportion of 1:4. Nitric acid (1+19): mix nitric acid and pure water thoroughly according to the proportion of 1:19. Standard working solution of the chromium chloride : Weigh 2.0 g potassium dichromate reference materials (accuracy to 0.1 mg), and put it in a 300 ml beaker, add 150 mL pure water, heat the beaker and make the sample solution slightly boiling on an electric stove for 10 min. After the solution is cool down to the room temperature, transfer the solution into a 500 ml volumetric flask and add 10 ml nitric acid (1+4) and pure water to the scale.Then we can separately pipette the standard working solution of the chromium chloride with volume 5mL、 10mL、 15mL、 20mL、 30mL、 40mL、 50mL、 60mL、 70mL and 80mL into ten 100 mL volumetric flasks, and add nitric acid (1+19) 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 Concentrations of series standard working solutions of chromium

g/L

NO.	Mass concentration (g/L)	Fluorescence intensity (cps/mA)
N_1	0.0360	53.99
N_2	0.0721	108.17
N_3	0.1081	155.72
N_4	0.1442	199.95
N_5	0.2163	299.58
N_6	0.2883	386.62
N_7	0.3604	503.31
N_8	0.4325	601.42
N_9	0.5046	701.26
N_{10}	0.5767	794.53

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 1.5 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 20 min. Filter the solution through filter paper to an 0.5L volumetric flask, wash the beaker and the filter paper several times with pure water, and add 20mL Nitric acid (1+4) 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	Aluminum
Collimator	8.8mm
Voltage	12v
Electric current	Auto
Analysis time	50s
Count rate	Medium
Atmosphere	Air
Matrix effects	Not considered
Energy range	0～20kev
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_{10} 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 chromium 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 chromium element in the sample can be calculated as mass fraction *W* and its value shown in% according to the following formula.

$$\omega = \omega_0 \times \frac{1.5}{m} \times \frac{V}{500}$$

Where: ω_0—the content of the chromium 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 chromium in the sample, expressed in %.

1.5—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 pure water 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 chromium element and affect the accuracy of the test. On the contrary, if pure water are used as the solvents, only the hydrogen and oxygen elements are introduced to the sample solution. So, the other elements would have little matrix effects on the chromium element and can be basically ignored.

Selection of standard solution.

Considering that all the most of the chromium element come from potassium chromate and potassium dichromate in pyrotechnics used for fireworks and firecrackers. In order to make the standard solution as consistent as possible with the sample solution, the K-Cr standard solution would be selected to make the working curve. It proved that when the concentration of the chromium element is controlled to the range of 0.03g/L∼0.58g/L, it would have little matrix effects on the chromium element and can be basically ignored. Because the contents of other impurity elements such as sodium and manganese are all mostly less than the chlorine element, they would also have little matrix effects on the chromium 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 chromium reference standard substance to some actual pyrotechnic samples, dissolved the samples and determined the contents of chromium in the sample solution. The values of the chromium 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	Chromium content of nominal (%)	Chromium content of measurment (%)	recovery rate（%）
1	BlacCr powder	Cr01	2.11	2.01	95.26
2	Lifting charge	Cr02	3.22	3.11	96.58
3	Bursting charge	Cr03	4.13	3.97	96.13
4	Chromium standard solution	Cr04	5.12	5.01	97.85
5	Chromium standard solution	Cr05	6.13	5.93	96.74
6	Chromium standard solution	Cr06	7.18	7.01	97.63
7	Chromium standard solution	Cr07	8.12	7.93	97.66
8	Chromium standard solution	Cr08	9.13	8.96	98.14
9	Chromium standard solution	Cr09	10.11	9.98	98.71
10	Chromium standard solution	Cr10	12.06	11.87	98.42
Average（X）					97.31
standard deviation (S)					1.04

Conclusions

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is used to determine the chromium content in pyrotechnics used for fireworCrs and firecracCrers, this method is accurate and quicCr with high accuracy and good precision. When the chromium content in the sample is in the range of 2%～12% as mass fraction, the recovery is 95.26%～98.71%.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 fireworCrs and firecracCrers industry.

Acknowledgement

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