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Determination of barium content in barium carbonate 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 barium content in barium carbonate 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 barium with high content, the sample solution must be highly diluted, and it must produce errors in measurement and call into question the reliability of the data. The method mentioned in this paper is about the determination of barium content in barium carbonate used for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometry by controlling matrix effects between elements. Using sample solution of barium carbonate in specific concentrates, the barium 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 barium in barium carbonate 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 98.37%～99.28%, 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 barium 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. Barium carbonate is one of the most popular chemical material used for fireworks and firecrackers. And the price of the barium carbonate depends on the content of the barium. Quantitative analysis method of the barium 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

Considering the weight of the sample is 0.5 g,constant volume is 1 L and the concentrations of the barium would be controlled in 0.30 g/L～0.40 g/L in sample solutions. And it can prove that when the barium content in the solution is in the range of 0.15 g/L～0.73g/L, there would be little matrix effects among elements. So we can establish a working curve which contains the barium elements with the content of 0.15 g/L～0.73 g/L to determine the barium 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 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 nitric acid 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 barium elements. The actual content of barium element in the sample can be calculated from the concentrations of the barium 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 barium nitrate: Weigh 3.0 g high purity barium nitrate powder 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, add 10 mL nitric acid (1+1) and 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 barium g/L

NO.	Mass concentration (g/L)	Fluorescence intensity (cps/mA)
N_1	0.1578	112.70
N_2	0.3156	268.32
N_3	0.4103	303.10
N_4	0.4735	395.50
N_5	0.6313	473.97
N_6	0.7260	539.56
N_7	0.7891	580.54
N_8	0.9469	697.17

Instrument and apparatus

Oven with accuracy to ±2°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.

Operation step

(1) Weigh the sample of about 0.5 g, accuracy to 0.1 mg.
(2) Place the sample into a clean 300 mL beaker, add 50 mL nitric acid (1+1) 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 to an 1 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	Thick Cu
Collimator	8.8mm
Voltage	50v
Electric current	Auto
Analysis time	35s
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 barium 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 barium element in the sample can be calculated as mass fraction *W* and its value shown in% according to the following formula.

$$\omega = \omega_0 \times \frac{0.5}{\mathrm{m}} \times \frac{V}{1000}$$

Where: ω_0—the content of the barium 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 barium in the sample, expressed in %.
0.5—assume that quantity of the sample, expressed in milligrams (g).
1000—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 barium 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 barium element and can be basically ignored.

Selection of standard solution.

In order to make the standard solution as consistent as possible with the sample solution, the barium standard solution would be selected to make the working curve. It proved that when the concentration of the barium element is controlled to the range of 0.15 g/L～0.73 g/L, it would have little matrix effects on the barium element and can be basically ignored. Because the contents of other impurity elements such as aluminum and manganese are all mostly less than the barium element, they would also have little matrix effects on the barium element in the sample solution.

Recovery test

To assess the accuracy of the method, we used the reference substances to do the recovery test. We dissolved the reference substances and determined the contents of barium in the sample solution. The values of the barium 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	Barium content of nominal (%)	Barium content of measurment (%)	recovery rate（%）
1	Barium carbonate	Ba 01	69.1	68.6	99.28
2	Barium carbonate	Ba 02	65.4	64.9	99.24
3	Barium carbonate	Ba 03	68.3	67.8	99.27
4	Barium standard solution	Ba 04	30.6	30.1	98.37
5	Barium standard solution	Ba 05	40.5	40.1	99.01
6	Barium standard solution	Ba 06	50.6	50.1	99.01
7	Barium standard solution	Ba 07	60.9	60.4	99.18
Average（X）					99.05
standard deviation (S)					0.30

Conclusions

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is used to determine the barium content in barium carbonate used for fireworks and firecrackers, this method is accurate and quick with high accuracy and good precision. When the barium content in the sample is in the range of 30%～70% as mass fraction, the recovery is 98.37%～99.28%.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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