Determination of potassium content in potassium perchlorate used for fireworks and firecrackersbased on Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF）

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Abstract. Methods used for the determination of potassium content in potassium perchlorate 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 potassium with high content,the sample solution must be highly diluted,and it mustproduce errors in measurement and calling into question the reliability of the data.The method mentioned in this paper is about the determination of potassium content in potassium perchlorate used for fireworks and firecrackers based on energy dispersive X-ray fluorescence spectrometry by controlling matrix effects between elements.Using samplesolution of potassium perchlorate in specific concentrates,the potassium content can be determinedby the specificcalibration curve established with an intensity calibration.This method can provide high accuracy and good precision in a short time with a simple process byefficiently controlling the matrix effects.It can fully meet the requirements forthe determination of potassium in potassium perchlorateused for different kinds of fireworks and firecrackers around the world,and ithas good generalization and practicability.The average recovery of the method can be96.49%～99.63%, 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 potassium 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. Potassium perchlorate is the most popular chemical material used to be oxidant in fireworks and firecrackers.Quantitative analysis method of the potassium 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

Concept of the method: considering the weight of the sample is 1.5g,constant volume is 0.5L and the concentrations of the potassium would be controlledin 0.70g/L～0.80g/L in sample solutions. And it can prove that when the potassium content in the solution is in the range of 0.16 g/L～0.99g/L and the chlorine elementswith the content of 0.18 g/L～1.10g/L, there would be little matrix effects among elements. So we can establish a working curve which contains the potassium elements with

the content of 0.16 g/L～0.99g/L and the chlorine elementswith the content of 0.18 g/L～1.10g/L to determine the potassium 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℃–55℃ and dried for 4 hours, and then placed into a dryer for cooling down to room temperature. Pretreated sample is fully dissolved in 150mL pure water and then filtered into volumetric flask as sample solution. The sample solution can beput into the sample cup and placed in the tank of the EDXRF to measure the fluorescence intensity of the potassium elements. The actual content of potassium element in the sample can be calculated from the concentrations of the potassium 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 andpure water thoroughly according to the proportion of 1:4. Nitric acid (1+19): mix nitric acid andpure water thoroughly according to the proportion of 1:19.Standard working solution of the potassiumchloride : Weigh 3.5g potassium chloride reference materials (accuracy to 0.1 mg), and put it in a 300 ml beaker, add 150mLpure water, heat the beaker and make the sample solution slightly boiling onan electric stovefor 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 potassiumchloride with volume 5mL、10mL、15mL、20mL、25mL and 30mL into six 100mLvolumetric 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 potassium
g/L

element	concentrations of series standard working solutions					
	N1	N2	N3	N4	N5	N6
K	0.1658	0.3316	0.4974	0.6632	0.8289	0.9947
Cl	0.1828	0.3657	0.5485	0.7314	0.9142	1.0970

Instrument and apparatus

Oven with accuracy to ±2℃. Analytical balance with accuracy to 0.1 mg. Energy dispersive X-ray fluorescence spectrometer (EDXRF): The 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 150mL 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 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 2Parameters of the EDXRF instrument

Filter	Fiber
Collimator	8.8mm
Voltage	12v
Electric current	Auto
Analysistime	35s
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_6 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 potassium 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 potassium 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 potassium 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 potassium in the sample, expressed in %.
1.5—assume thatquantity 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

Selection of standard solution.

Considering that all the potassium element come from $KClO_4$. In order to make the standard solution as consistent as possible with the sample solution,the K-Cl standard solution would be selected to make the working curve. It proved that when the concentration of the potassium element is controlled to the range of 0.16 g/L～0.99g/L and the chlorine elementwith the content of 0.18 g/L～1.10g/L,itwould have little matrix effects on the potassium element and can be basically ignored.Because thecontents of other impurity elements such as lsodium and manganese are all

mostly less than the chlorine element,they wouldalso have little matrix effects on the potassium elementin the sample solution.

Recovery test

To assess the accuracy of the method, we used different standard substances and serious potassium standard solutions to do the recovery test. We dissolved the samples and determined the contents of potassium in the sample solution. The values of the potassium 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	Potassium content of nominal (%)	Potassium content of measurment (%)	recovery rate（%）
1	Potassium perchlorate	K01	24.95	24.71	99.04
2	Potassium perchlorate	K02	25.13	24.87	98.97
3	Potassium perchlorate	K03	25.39	24.97	98.35
4	Potassium standard solution	K04	7.12	6.87	96.49
5	Potassium standard solution	K05	11.41	11.11	97.37
6	Potassium standard solution	K06	14.25	13.94	97.82
7	Potassium standard solution	K07	21.38	21.12	98.78
8	Potassium standard solution	K08	38.5	38.29	99.45
9	Potassium standard solution	K09	57.76	57.41	99.39
10	Potassium standard solution	K10	61.44	61.21	99.63
Average（X）					98.53
standard deviation (S)					0.97

Conclusions

Energy dispersive X-ray fluorescence spectrometry (EDXRF) is used to determine the potassium contentin potassium perchlorate used for fireworks and firecrackers,this method is accurate and quick with high accuracy and good precision. The recovery is 96.49%～99.63%.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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