Determination and Chemometrics of Sulfur in Pyrotechnic Composition by GC-MS

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Abstract: Gas chromatography-mass spectrometry (GC-MS) was used to determine the sulfur in 25 pyrotechnic compositions of crackers. Analysis of Variance (ANOVA) and Least Significant Difference-t test (LSD-t test) were used to study the contents of sulfur of pyrotechnics from different sources. The results showed that no sulfur was detected in some pyrotechnics, and the detected sulfur content ranged from 8.7-53.9μg /mg. The content of sulfur in different manufacturers and different types of pyrotechnics varied greatly, which 83.3 % of pyrotechnic compositions can be accurately identified. This study shows the potential for further integration with other analytical methods for pyrotechnic drug tracing studies and will provide intelligence information for the source of pyrotechnics in explosion cases, and useful reference for the rapid detection of such cases.

Keywords: Pyrotechnics; GC-MS; Sulfur; Chemometrics; Traceability

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1. Introduction

China is the world's largest producer, consumer, and exporter of fireworks and firecrackers, accounting for approximately 90% of global production. Its products are exported to nearly 100 countries and regions worldwide[1]. Pyrotechnic composition is widely used, inexpensive, and readily available, making it a common explosive ingredient in homemade explosives. The analysis and testing of Pyrotechnic composition are of great significance for the investigation and safety assessment of explosive incidents [2,3].Sulfur(elemental sulfur) is a yellowish powder with a melting point of 119°C and is an important component of Pyrotechnic composition. As people become more concerned about the safety of transportation as well as urban environmental protection, there has been a

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gradual shift towards low-sulfur or sulfur-free types of pyrotechnic composition with sulfur content generally not exceeding 5% [4].In the field of forensic science research on pyrotechnic composition mainly focuses on qualitative detection methods for various oxidants. Common methods include Scanning Electron Microscopy / Energy Dispersive X-ray Spectroscopy (SEM/EDS)[5,6], X-ray Diffraction (XRD)[7], Fourier Transform Infrared Spectroscopy (FTIR)[8], Raman Spectroscopy (Raman)[9], Ion Chromatography (IC)[10], Capillary Electrophoresis (CE)[11]. Among these methods SEM/EDS and XRD can qualitatively detect sulfur but due to its low content accurate quantification remains challenging[12]. However, sulfur plays an important role in fireworks compositions. Even small variations in its proportion can significantly affect the combustibility and ignition temperature of mixtures. When present in high proportions, it produces special smoke effects when released from yellowish smoke. In order to achieve different acousto-optic effect, the ratio of sulphur in firework compositions varies greatly[13]. Therefore, a precise quantitative analysis of sulphur components in fireworks can be inferred to determine their type, differentiate between different sources, and provide crucial intelligence information for case investigations as well as key evidence for court litigation.

Current literature on sulfur component analysis primarily focuses on mineral and building material substrates, with limited research on sulfur in explosives. In 2005, Bradley et al first employed gas chromatography-mass spectrometry for the qualitative examination of trace sulfur in inorganic explosives and residues, achieving a sensitivity 400 times greater than traditional colorimetric methods[12]. Huang et al. developed a quantitative method for detecting sulfur in black powder using gas chromatography-mass spectrometry, with detection and quantification limits of 0.65 μg/mL and 2.17 μg/mL respectively, meeting practical analytical requirements[13]. Compared to black powder, pyrotechnic composition have more complex components with variable proportions of sulfur. This study utilized gas chromatography-mass spectrometry to quantitatively detect sulfur in Pyrotechnic composition, examined interference factors from solvent extraction substrates, optimized sample pretreatment methods, and applied chemometric techniques like ANOVA and LSD-t tests to explore traceability technology for fireworks.

2. Materials and Methods

(1) Instrument and reagents

GCMS-QP2020 (Shimadzu Company, Japan); METTLER TOLEDO MS205DU Electronic Analytical Balance (Mettler Company, Switzerland); KQ-250DB Ultrasonic Cleaner (Kunshan Ultrasonic Instrument Company, Kunshan); DT5-3 Centrifuge (Beijing Times Beili Centrifuge Company, Beijing)

Sulfur, Carbon disulfide, Chloroform, Ethanol, Hydrochloric acid (Sinopharm Chemical Reagent Company); Ultrapure water(18.2 MΩ cm-1)

1.00 mg solid standard material of elemental sulfur was dissolved in 1.00 mL chloroform to obtain 1 mg/mL mother liquor of sulfur. Diluted with chloroform step by step to a standard solution of 5.0, 10.0, 50.0, 100.0, 200.0, 500.0 μg/mL.

(2) Sample preparation and experimental design

All the inspected materials come from the fireworks and firecrackers contraband confiscated in the cases. Minimum individual package used within this article and profile of S21 as shown in Figure 1. The samples S20-S22 are double-sounding and contain two kinds of pyrotechnic composition.

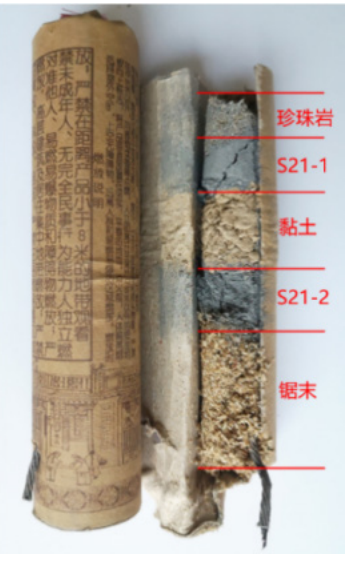

Fig.1 Minimum individual package used within this article and profile of S21

The materials were disassembled with scalpel, and the pyrotechnic compositions were sifted (74μm) to remove large particle impurities, and 25 samples were obtained.

25 samples were prepared according to follow methods: (1) 10.00 mg of samples were dissolved in ultrapure water to produce a water-soluble portion and a water-insoluble portion. (2) water-insoluble portions were dissolved in hydrochloric acid (1+1) to produce a water-soluble portion and a water-insoluble portion, (3) water-insoluble portions were dissolved in chloroform to produce a solution. The blank experiment was carried out meanwhile.

(3) Instrumental Validations, Parameters, and procedures

Agilent DB-5 MS quartz capillary column (crosslinked methylsiloxane, 30 m*0.25 mm, film thickness 0.25 μm) was used.

Table 2 Parameters of GC-MS

GC Parameter	Mwasure	MS Parameter	Measure
Injection Volume	1 μl	Transfer Line Temperature	230 ℃
Injector Temperature	240 ℃	Source Temperature	230 ℃
Flow Rate	240 ℃	Quad Temperature	150 ℃
Initial Temperature	40 ℃	Scan Mode	SIM
He Flow/(mL/min)	1.0 ml/min	MS Range	m/z 30-330
Ramp 1	10℃/min to 80 ℃		
Hold Time 1	2 min		
Ramp 2	10℃/min to 240 ℃		
Hold Time 2	5 min		
Total Run Time:	25 min		

3. Results and Discussion

(1) Pretreatment optimization

The commonly used extraction solvents for sulfur in literature include carbon disulfide, chloroform, ethanol, acetone, etc. In this paper, the extraction effect of each solvent on sulfur was investigated. The results showed that elemental sulfur dissolved rapidly and fully in chloroform at room temperature. Because of the complexity of pyrotechnic composition, the content of sulfur is low, and there are water-soluble oxidant agents, such as

potassium perchlorate and barium nitrate; metal reducing agents, such as aluminum powder, magnesium aluminum alloy; other contents, such as colorants, adhesives and stabilizers. Therefore, three-steps extraction (ultrapure water, hydrochloric acid and chloroform) were adopted in this paper to Optimize the pretreatment method.

(2) Methodological investigation

Under the conditions listed in section 2.3, standard curve analysis was performed, the concentration of standard sulfur solution as the horizontal coordinate, the peak area of S8 as the vertical coordinate. The regression equation was y = 1441.3x-10575, the linear range was 0 ~ 500μg /ml, and the linear correlation coefficient r^2 = 0.999. The Limit of Quantitation (LOD = 1.62) calculated with S/N = 3, and the Limit of Quantitation (LOQ = 5.42) calculated with S/N = 10. The standard solution was tested for 6 consecutive times to investigate the repeatability of the method, indicating that the method has good repeatability. The experimental results are shown in Table 2. The recoveries of all elements were between 90% and 110%.

Table 1 Repeatability of the method

Numbe	Peak area	S concentration (μgm/L)	Standard deviation (SD)	RSD/%
01	268606	196.2	3.94	2.0
02	270370	194.8		
03	270297	194.9		
04	269843	195.3		
05	284046	204.4		
06	268506	193.6		

(3) Sample testing and data analysis

As shown in Figure 2, S_8 peak at 23.275 min retention time, S_6 peak at 17.207 min retention time. The small amount of S_6 is produced by sulfur itself or the decomposition product of S_8 at high temperature.

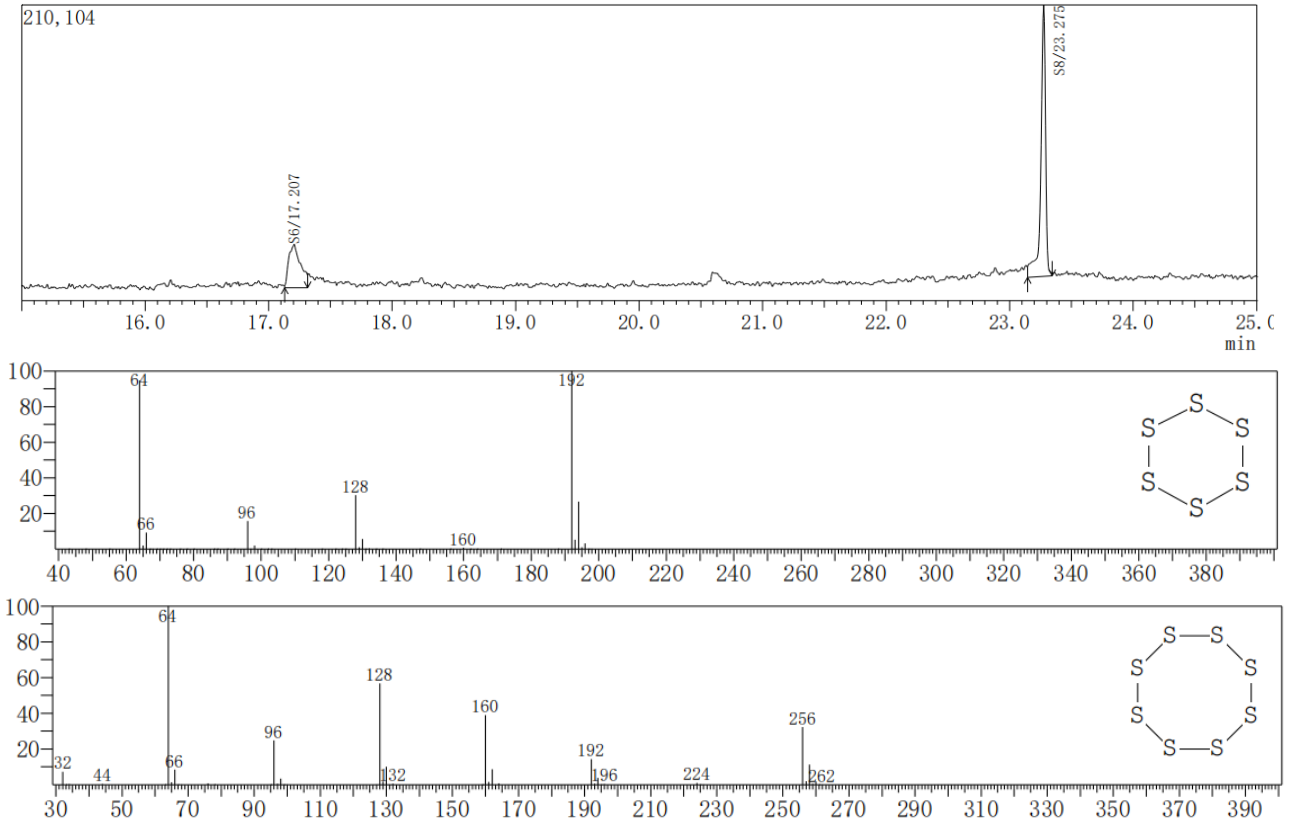

Fig.2 Selective ion chromatograms(m/z=64)of the standard solutions of sulfur and the mass spectra of S_6 and S_8

According to the conditions listed in Section 2.3, 25 samples were tested, and no sulfur was detected in S19, while the content of sulfur detected in other samples ranged from 8.7 μg/mg to 53.9 μg/mg. The content of sulfur in different manufacturers and different types of pyrotechnic composition varied greatly. The content of sulfur in sample S01-S18 (Group A) ranged from 8.7-32.0μg/mg, and sample S20-S22(Group B) ranged from 26.7-53.9μg /mg, showing significant differences between the two groups, as shown in Figure 4. Analysis of mean variance (ANOVA) and minimum significant difference t-test (LSD-t test) were performed on 24 samples. It was found that the difference between the two groups was obvious, and the sample in Group A and Group B could be respectively distinguished by 100% and 73.7%, the overall distinction rate was 83.3%.

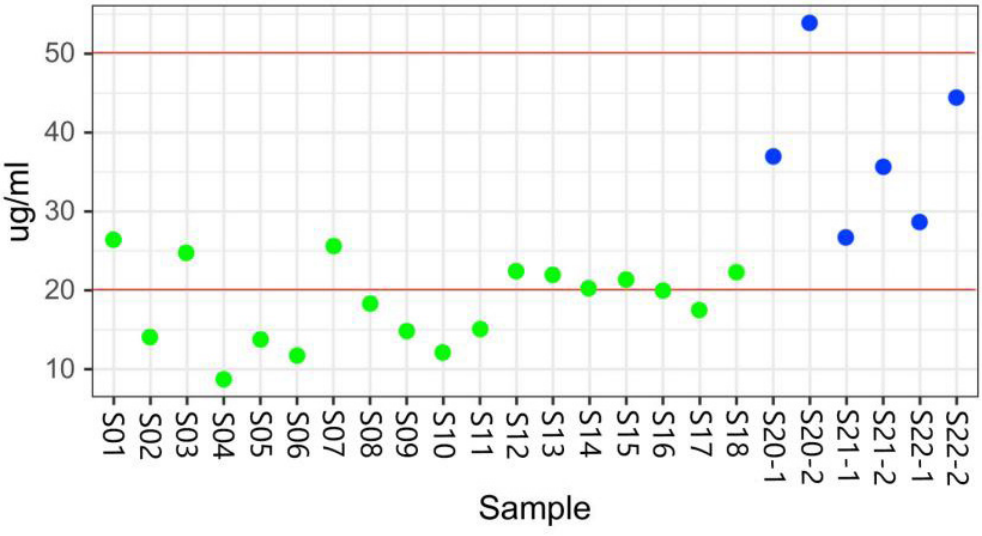

Fig.3 Comparative analysis of average concentration in the detected samples used within this article

4. Conclusions

The content of sulfur in pyrotechnic powder is very different, which has a great relationship with the function of fireworks and the preparation technology of manufacturers. In this study, water and acid were used for sample pretreatment to eliminate the interference of other components on the determination of sulfur content. The elemental sulfur content in 25 kinds of fireworks samples collected by public security organs was determined by GC-MS. The data of sulfur content were analyzed by means of similarity analysis of variance (ANOVA) and minimum significant difference T-test (LSD-t test), and it was found that 83.3% of pyrotechnic samples had significant differences, which could distinguish the source of pyrotechnic composition, indicating the potential of further combining other analytical methods for pyrotechnic composition traceability research.

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