

**Determination of Elemental Sulfur in Explosives and
Explosive Residues by Gas Chromatography-Mass Spectrometry**

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Abstract

A method for the positive identification of elemental sulfur in explosives and explosive residues is presented. Following a carbon disulfide wash of explosives or explosive residues, a sample of the extracted material is injected onto a gas chromatography (GC) column, then analyzed via mass-selective (MS) detection. A positive identification of elemental sulfur is based on both retention time and fragmentation pattern. The GC-MS method is demonstrated to be useful in detecting and positively identifying elemental sulfur from both burned and unburned explosive mixtures. With a detection limit of 2.5 ng of elemental sulfur on the column, this method is 400 times more sensitive than the presumptive chemical color test that has previously been the method employed for the detection of small amounts of sulfur. (*J. Forensic Sci.*, 2005:50,96-103.)

Introduction

Elemental sulfur is commonly used as a fuel component in inorganic explosive mixtures such as black powder, flash powder, and a variety of black powder substitutes. Consequently, residues from such explosive mixtures also contain elemental sulfur. When analyzing these residues, positive identification of elemental sulfur, in conjunction with other characteristic reaction products, is essential in determining the composition of the originating explosive mixture. In many instances, however, only a very small amount of elemental sulfur is recovered, thereby limiting the options of analysis technique for positive identification. Currently, the most

commonly used techniques are X-ray diffractometry (XRD), energy dispersive X-ray analysis (EDX), and a chemical color test. Although both XRD and EDX require relatively small amounts of solid sample for analysis, it is often much greater than what can be isolated from an explosive residue. Thus, the chemical color test—which requires far less sample than XRD or EDX—is frequently utilized.

In 2001, the Technical Working Group for Fire and Explosions (TWGFEX) released an action document (1) suggesting that the chemical color test for sulfur is insufficient for the positive identification of elemental sulfur in explosives and explosive residues. This means that the chemical color test cannot be the sole analytical technique used to determine the presence of sulfur. Consequently, an alternative method for the positive identification of elemental sulfur was sought.

In this study, which has been published previously (2), GC-MS is shown to be capable of positive identification of elemental sulfur in explosives and explosive residues, and to be 400 times more sensitive for sulfur than the chemical color test.

Methods

GC-MS analyses were performed on an Agilent 6890 GC coupled with an Agilent 5973 MS detector. A 25 m Agilent HP-1 capillary column (cross-linked methyl siloxane, 0.2 mm I.D., 0.5 μ m film thickness) was used with helium as the carrier gas, with a flow rate of 1.0 mL/min. Several combinations of GC-MS settings were tested in order to determine an optimized method for sulfur analysis, resulting in the following: injector port, 250°C; MS interface, 280°C; MS source, 200°C; initial column T, 230°C; initial hold time, 6 min; T ramp, 10°C/min to 250°C; final hold time, 2 min; split ratio, 40:1; MS scan mode, electron ionization; ionization energy, 70eV; solvent delay, 2 min; MS scan range, 30-330m/z; total run time, 10

min; retention time of elemental sulfur peak, 5.3 min.

Samples were analyzed for S_8 , the most thermodynamically stable allotrope of elemental sulfur. (3) Test samples were prepared by performing a carbon disulfide (CS_2) wash of the explosive or explosive residue. The CS_2 was then allowed to evaporate completely, in order to confirm insufficient material to perform other instrumental tests for sulfur. For GC-MS analysis, the CS_2 extract was dissolved in ~ 0.5 mL CS_2 , and then transferred to a shell vial. This solution was then evaporated to a small volume (~ 50 μL), and a 1 μL sample was injected into the GC-MS. Positive identification of sulfur was based on retention time and identification of the fragmentation pattern for S_8 . Fragmentation patterns were compared to an in-house reference for S_8 and to references in the Wiley database (4), using a probability-based matching search routine. The search result statistics include a value called “match quality,” which in general refers to the probability that the sample spectrum has been identified correctly. Match quality values greater than 90 are considered very good matches, while values less than 50 suggest substantial differences between the sample and the reference spectra (5). For this study, a positive identification of sulfur required a match quality value of 90 or greater. For chemical color test analysis, the CS_2 extract was dissolved in ~ 0.5 mL pyridine, swirled gently by hand to mix, and then warmed on a hot plate at $\sim 150^\circ\text{C}$ for ~ 1 min. Then one drop of 2 N NaOH was added, and any color change was noted. A positive identification of sulfur was based on a color change to any hue ranging from very pale blue to deep blue-greenish brown. (6)

Results and Discussion

Identification of Elemental Sulfur from Explosives and Explosive Residues

In order to investigate the potential use of GC-MS as a method of detecting and positively identifying elemental sulfur as part of explosives analysis, samples of unburned and

burned explosive mixtures were examined. The two explosive mixtures chosen for this study were a flash powder (composed of potassium chlorate, sulfur, and aluminum) and Pyrodex (a black powder substitute composed of potassium perchlorate, potassium nitrate, sulfur, carbon, sodium benzoate, and cyanoguanidine).

Samples of unburned flash powder (20 mg) and Pyrodex (50 mg), and samples of burned flash powder (320 mg before burning) and Pyrodex (300 mg before burning), were extracted with CS₂ and processed as described previously. In no instance was there sufficient extracted material to perform XRD or EDX analysis. Figure 1 presents data for Pyrodex only. Figures 1(A) and 1(C) are the total ion current chromatograms (TICs) for unburned and burned Pyrodex. For unburned Pyrodex, there is one large peak with a retention time of ~5.3 min, and its fragmentation pattern is shown in Figure 1(B). The peak is positively identified as " -S₈, with a match quality value of 96. For burned Pyrodex, there is a small peak at ~5.3 min that is superimposed upon a broad, noisy background envelope of peaks. The fragmentation pattern for this peak is shown in Figure 1(D). Although this fragmentation pattern also contains many contributions from the background envelope of peaks, fragments indicative of sulfur are clearly visible, and " -S₈ is positively identified with a match quality value greater than 90. Following analysis by GC-MS, the remaining extracted material from each sample was tested for elemental sulfur using the chemical color test. The chemical color test confirmed the presence of sulfur in every sample.

It should be noted that the fronting of the peak at ~5.3 min in the TIC for unburned Pyrodex is commonly seen when relatively large amounts of sulfur are loaded onto this particular column. However, the fronting does not interfere with the ability to positively identify " -S₈. Diluting the sample would result in minimization of fronting.

Detection Limits

Detection limits for both the chemical color test and the GC-MS method were determined experimentally. In each case, the same standard sulfur stock solution was used. This stock solution was created by adding 5.0 mg precipitated sulfur powder to 25.0 mL CS₂. The resulting solution has a concentration of 7.8×10^{-4} M S₈ (200 ng S₈/μL solution).

The detection limit for the chemical color test for sulfur was determined using the sample preparation procedure as indicated previously. The blank control was a clean shell vial that was processed in the same manner as all of the trials, and the sulfur control was a known, but not quantified, sample of sulfur that was also processed in the same manner as all of the trials. All experimental observations were witnessed and confirmed by another analyst, in addition to the author. Table 1 summarizes the results, including the amounts of sulfur used and any observed color change. As indicated in the table, the smallest amount of sulfur that gave a positive result was 1 μg. Trials with 0.8 μg and 0.6 μg were inconclusive, meaning that either one or both of the analysts observing the experiment were unable to detect a definitive color change. Thus, the detection limit for the chemical color test for sulfur was determined to be 1 μg.

The detection limit for the GC-MS method for sulfur was determined by injecting various amounts of the standard sulfur stock solution in order to deliver 5 ng, 2.5 ng, and 1 ng of S₈ onto the column. The resulting TICs are shown in Figure 2. Wiley database searches were performed for the peak at ~5.3 min in each TIC. The peaks in both the 5 ng and 2.5 ng trials were positively identified as S₈, while the peak in the 1 ng sample was too weak to be positively identified. Thus, the detection limit for the GC-MS method for sulfur was determined to be 2.5 ng, making it 400 times more sensitive for elemental sulfur than the chemical color test.

The GC-MS detection limit for sulfur could be decreased even further by changing the instrument parameters and extending the total runtime. However, for the purpose of explosives analysis, a compromise between total runtime and detection limit was made.

Reproducibility

The reproducibility of the analytical method was tested by injecting 1.0 μL of the standard sulfur stock solution five times. For the five trials, the peak retention time ranged from 5.327–5.331 min, the abundance of the peak ranged from 33,000–43,000 counts, and the minimum match quality was 94. These data demonstrate that the sulfur peak consistently appears at a retention time of ~ 5.33 min, and that it is consistently positively identifiable by the Wiley database search criteria.

Although explosives analysis typically only requires identification of elemental sulfur and not quantification, it is interesting to note statistics regarding the abundance of the sulfur peak in each case. For the five trials, the mean for the abundance was 38,200 counts, and the standard deviation of the population was 3,022 counts. The relative standard deviation was found to be 8%.

Advantages and Limitations

The primary advantages of using GC-MS to identify elemental sulfur from explosives and explosive residues include the following:

1. It is an instrumental technique that does not require the human eye for detection, as is the case for the chemical color test.
2. It is a very sensitive technique. The GC-MS method as reported here is capable of detection and positive identification of as little as 2.5 ng of sulfur on the column, making it 400

times more sensitive than the chemical color test, which has a detection limit of 1 μg of sulfur.

3. It is a conclusive technique which allows the collection and archival of hard copy data to support or refute the positive identification of sulfur.

4. GC allows the separation of other compounds that may be present in the sample, and that can interfere with the chemical color test (e.g. organic dyes). Therefore, inconclusive results due to interference are minimized.

The only limitation of using GC-MS to identify sulfur from explosives and explosive residues that was uncovered during this study involved analysis time. The total time required for casework identification of sulfur (i.e. runs for sensitivity check, blank, and sample) is approximately two to three times longer than that for the chemical color test in instances where the chemical reagents necessary for the color test are already prepared. However, it can be nearly comparable in instances where fresh chemical reagents for the color test must be prepared. Moreover, in reference to the total explosives analysis procedure, which typically involves both a water and a CS_2 extraction of the residue, the GC-MS analysis for sulfur can easily be performed while waiting for the water extract to evaporate. Consequently, the use of GC-MS will not increase the total time necessary for a complete explosives case analysis.

Conclusion

This study has demonstrated GC-MS to be a very promising tool to replace the chemical color test in the detection and positive identification of elemental sulfur from explosives and explosive residues. Its use is recommended for cases in which there is insufficient material to perform XRD or EDX analysis. The GC-MS method is efficient, conclusive, and 400 times more sensitive for sulfur than the chemical color test.

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References

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Table 1. Data from determination of detection limit of chemical color test for elemental sulfur.

Amount of Sulfur Present	Observations
0 μg	Negative; no color
10 μg	Positive; blue
2 μg	Positive; light blue
1 μg	Positive; very pale blue
0.8 μg	Inconclusive
0.6 μg	Inconclusive
0.4 μg	Negative; no color

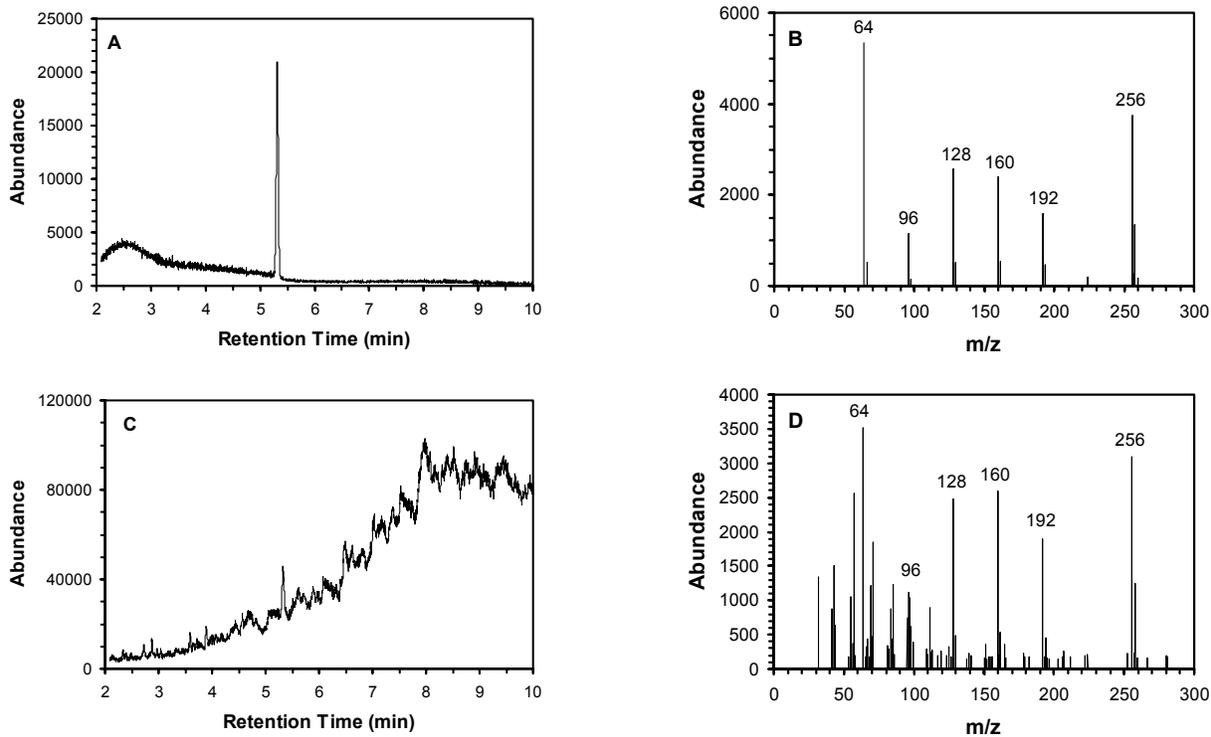


Figure 1. (A) TIC for sample solution from CS₂ extraction of unburned Pyrodex. (B) Fragmentation pattern for peak at retention time of 5.3 min in (A). (C) TIC for sample solution from CS₂ extraction of burned Pyrodex. (D) Fragmentation pattern for peak at retention time of 5.3 min in (C).

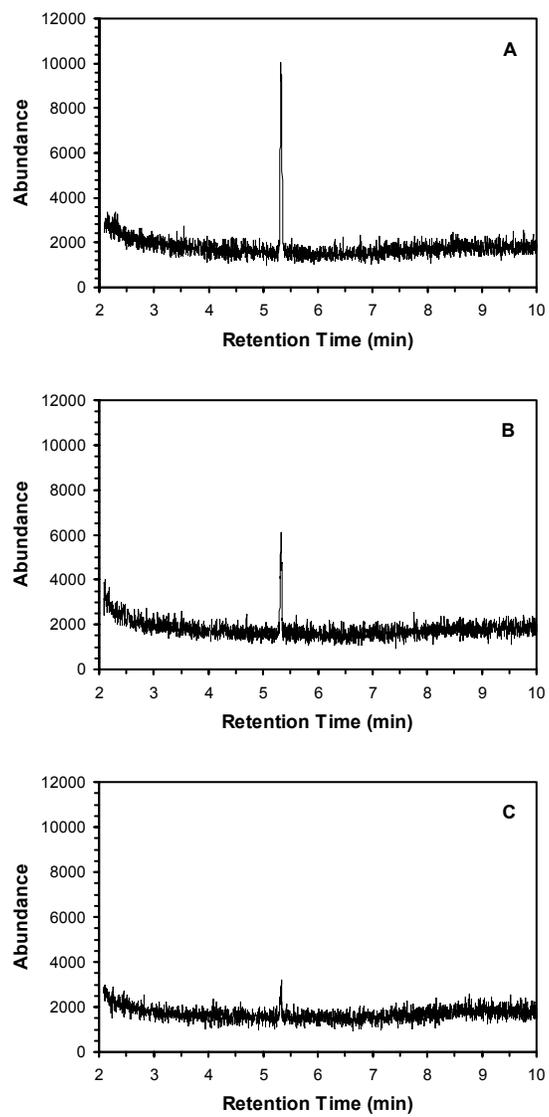


Figure 2. TICs for (A) 5 ng, (B) 2.5 ng, and (C) 1 ng of sulfur on the column.