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

**ABSTRACT:** A new method for the positive identification of elemental sulfur in explosives and explosive residues is developed. 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 ( $2.5 \times 10^{-9}$  grams) of elemental sulfur on the column, it is shown to be 400 times more sensitive than the presumptive chemical color test that is currently the method employed for detection of small amounts of sulfur.

**KEYWORDS:** forensic science, explosives analysis, gas chromatography-mass spectrometry, sulfur, inorganic explosive mixtures

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 identification 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, the necessary amount is often much greater than what can be isolated effectively from an explosive residue. Thus, the chemical color test—which requires far less sample than XRD or EDX—is frequently utilized. To perform the test, any suspected sulfur that is recovered from the explosive residue is dissolved in warm pyridine, and then a drop of concentrated sodium hydroxide solution is added. If elemental sulfur is present, the solution changes from colorless to a color ranging from very pale blue to deep blue-greenish brown, with the particular hue dependent upon the amount of sulfur that is present (1).

Recently, the Technical Working Group for Fire and Explosions (TWGFEX—a group sponsored by the National Center for Forensic Science, whose purpose is to promulgate and foster the development of national protocols, training, and quality assurance guidelines to assist personnel involved in fire and explosives analyses) released an action document (2) 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. Because the other accepted

analytical techniques (XRD and EDX) require greater sample amounts than are typically available from explosive residues, an alternative method for the positive identification of elemental sulfur has been sought.

One possible alternative analysis method is gas chromatography-mass spectrometry (GC-MS). In the past several years, GC-MS has been shown to be able to detect elemental sulfur from a very limited variety of samples. In 1997, Chen et al. (3) used GC-MS to identify and quantify elemental sulfur extracted from lake sediments. They reported having achieved an absolute detection limit of 96 pg ( $96 \times 10^{-12}$  grams) of elemental sulfur. Shortly thereafter, Gryglewicz and Gryglewicz (4) reported using GC-MS to determine the quantity of elemental sulfur in coal and related samples, but they did not perform detection limit studies. Most recently, Zhao (5) has used GC-MS to study elemental sulfur in naphtha and gasoline. However, to the best of the author's knowledge, no previous study has been performed to examine the possibility of using GC-MS to identify elemental sulfur as part of explosives analysis.

In the present article, 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 (Palo Alto, CA) gas chromatograph (model 6890) coupled with an Agilent quadrupole mass selective detector (model 5973). A 25 m Agilent HP-1 capillary column (crosslinked methyl siloxane, 0.2 mm I.D., 0.5  $\mu$ 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 parameter settings were tested in order to determine an optimized method for sulfur analysis, resulting in the following settings: injector port, 250°C; MS interface, 280°C; MS source, 200°C; initial column temperature, 230°C; initial hold time, 6 min; temperature ramp, 10°C/min to 250°C; final hold time, 2 min; split ratio, 40:1; MS scan mode, electron ionization; ionization energy, 70 eV;

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solvent delay, 2 min; MS scan range, 30–330 m/z; total run time, 10 min; retention time of elemental sulfur peak, 5.3 min. Selected data discussed below were collected using the GC-MS parameter settings for arson analysis, which differ from the parameter settings for sulfur analysis in the following ways: initial column temperature, 50°C; initial hold time, 2 min; temperature ramp, 8.5°C/min to 250°C; final hold time, 8 min; solvent delay, 3 min; MS scan range, 50–330 m/z; total run time, 33.53 min; retention time of elemental sulfur peak, 24.1 min.

Sample mass spectra were compared to reference mass spectra in the Wiley database (6), 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 (7).

Samples to be analyzed for sulfur content were prepared by performing a CS<sub>2</sub> wash of the explosive or explosive residue, and then allowing the CS<sub>2</sub> extraction to evaporate completely. For GC-MS analysis, the residual material was dissolved in 0.5–1.0 mL CS<sub>2</sub>, and the resulting solution was then transferred via Pasteur pipette to a shell vial. This solution was then evaporated to a small volume (~50–100 µL), and a 1 µL sample was injected into the GC-MS. A positive identification of sulfur was based on both retention time and MS fragmentation pattern. For chemical color test analysis, the residual material from the CS<sub>2</sub> extraction was dissolved in 0.5–1.0 mL pyridine, swirled gently by hand to mix, and then warmed on a hot plate at ~150°C for 60 s. 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.

Carbon disulfide (reagent grade), precipitated sulfur powder, pyridine (reagent grade), sodium hydroxide beads, pentane (spectral grade), acetone (reagent grade), and activated carbon (50–200 mesh) were all purchased from Fischer Scientific Co. (Pittsburgh, PA). Samples of Pyrodex and flash powder were obtained from a collection of explosive mixtures maintained by the Illinois State Police.

## Results and Discussion

### *Theoretical Background*

The idea of using GC-MS to identify elemental sulfur originates from observations made while performing routine arson analyses. When using the dynamic activated charcoal elution (ACE) technique (a method used to collect and concentrate vapors from flammable liquids), a “blank” is created by eluting an activated charcoal tube with 0.5 mL carbon disulfide (CS<sub>2</sub>). These blanks are analyzed by GC-MS and give rise to a total ion current chromatogram (TIC) relatively devoid of peaks, except for one strong peak (Fig. 1a). This peak consistently results in positive identification (match quality = 96) as “octa-sulfur” based on a search of the Wiley database (6) for a match to the MS fragmentation pattern (Figs. 1b and 1c). “Octa-sulfur” is actually  $\alpha$ -S<sub>8</sub> (henceforth referred to as S<sub>8</sub>)—the most thermodynamically stable allotrope of elemental sulfur (8). The consistent observation of elemental sulfur in the arson blanks prompted two important questions: [1] what is the origin of the sulfur in these blanks, and [2] if GC-MS can identify sulfur in these blanks, could it also identify sulfur isolated from explosives and explosive residues? Question [1] will be addressed

in this section, and the remainder of the article will be devoted to addressing Question [2].

In order to address the question of the origin of sulfur in the arson blanks, the CS<sub>2</sub> and charcoal used in the creation of the blank were analyzed separately. Both neat CS<sub>2</sub> and a sample of 0.5 mL neat CS<sub>2</sub> concentrated by evaporation to less than one drop (~50 µL) were analyzed for the presence of elemental sulfur using GC-MS; however, no sulfur was detected in either case. Therefore, the CS<sub>2</sub> itself is not the origin of the sulfur in the arson blanks. To check for sulfur in the activated charcoal, blank tubes were prepared and then eluted with pentane, acetone, or pyridine, rather than CS<sub>2</sub>. Sulfur is soluble in pyridine and slightly soluble in pentane and acetone (9), so these solvents are capable of collecting any sulfur that may be present in the activated charcoal. None of the tubes eluted with these solvents resulted in a TIC containing sulfur; therefore the activated charcoal itself is not the origin of the sulfur in the arson blanks. It is important to note that the property of the charcoal being activated is significant. Upon elution with CS<sub>2</sub>, charcoal that had not been treated to become activated gave a TIC that did not contain sulfur.

The aforementioned results suggest that the origin of elemental sulfur observed in the arson blanks is a direct result of the interaction of CS<sub>2</sub> with the activated charcoal. Furthermore, basic surface chemistry principles, along with these experimental observations, lead to the hypothesis that this interaction would take the form of a surface-catalyzed decomposition of CS<sub>2</sub>, followed by formation of S<sub>8</sub> through surface-enhanced reactions. The newly formed S<sub>8</sub> would then be desorbed by CS<sub>2</sub> when the solvent is forced through the tube to collect the blank. A search of the literature revealed no previous research to either support or refute this hypothesized mechanism, so it is a potentially promising avenue for future research.

The remaining sections of this article will address the use of GC-MS as a means of positively identifying sulfur from explosives and explosive residues.

### *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).

Unburned samples of flash powder (20 mg) and Pyrodex (50 mg) were extracted with CS<sub>2</sub> and processed as described previously. In neither case was there sufficient extracted material to perform XRD or EDX analysis. Figure 2 shows the TICs for each sample. In both cases, there is one peak with a retention time of ~5.3 min, which is positively identified as elemental sulfur (for flash powder, match quality = 95; for Pyrodex, match quality = 96). The fronting of this peak in both cases is commonly seen when relatively larger amounts of sulfur are loaded onto this particular column, but it does not interfere with the ability to positively identify the sulfur peak. Diluting the sample would result in minimization of fronting. The remaining extracted material in each case was then tested for elemental sulfur using the chemical color test, which in both cases confirmed the presence of sulfur.

Next, burned samples of flash powder (320 mg, unburned) and Pyrodex (300 mg, unburned) were extracted with CS<sub>2</sub> and

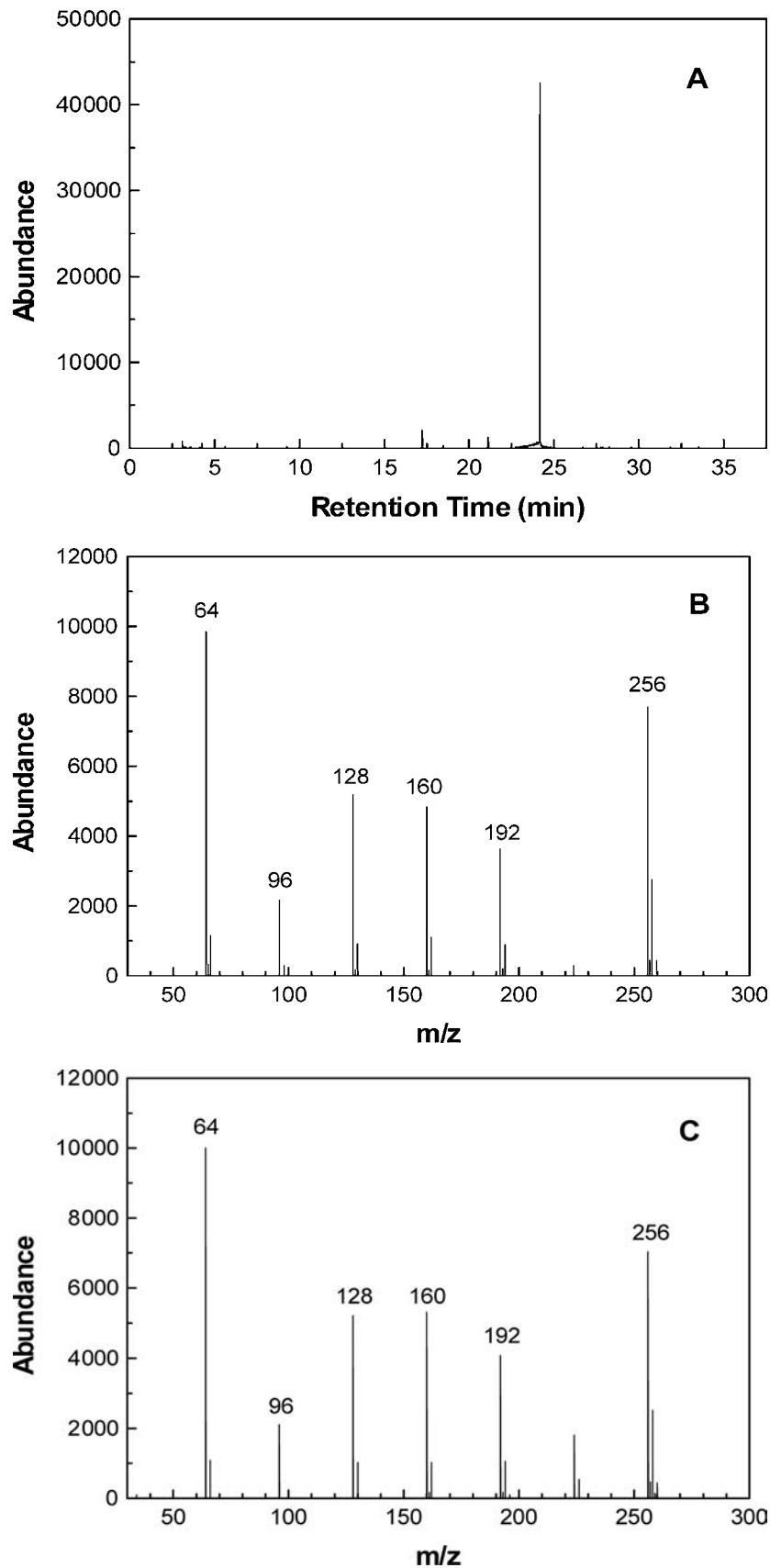


FIG. 1—(a) Total ion current chromatogram (TIC) for sample solution resulting from elution of activated charcoal tube with carbon disulfide ( $CS_2$ ). The peak with a retention time of 24.18 min is elemental sulfur ( $S_8$ ). Note that this TIC was collected using the standard instrument parameters for arson analysis. (b) Fragmentation pattern for peak at retention time of 24.18 min in (a). Note that fragments with m/z below 50 were not recorded. (c) Best match (match quality = 96) from Wiley database search for fragmentation pattern in (b), indicating positive identification of  $S_8$ .

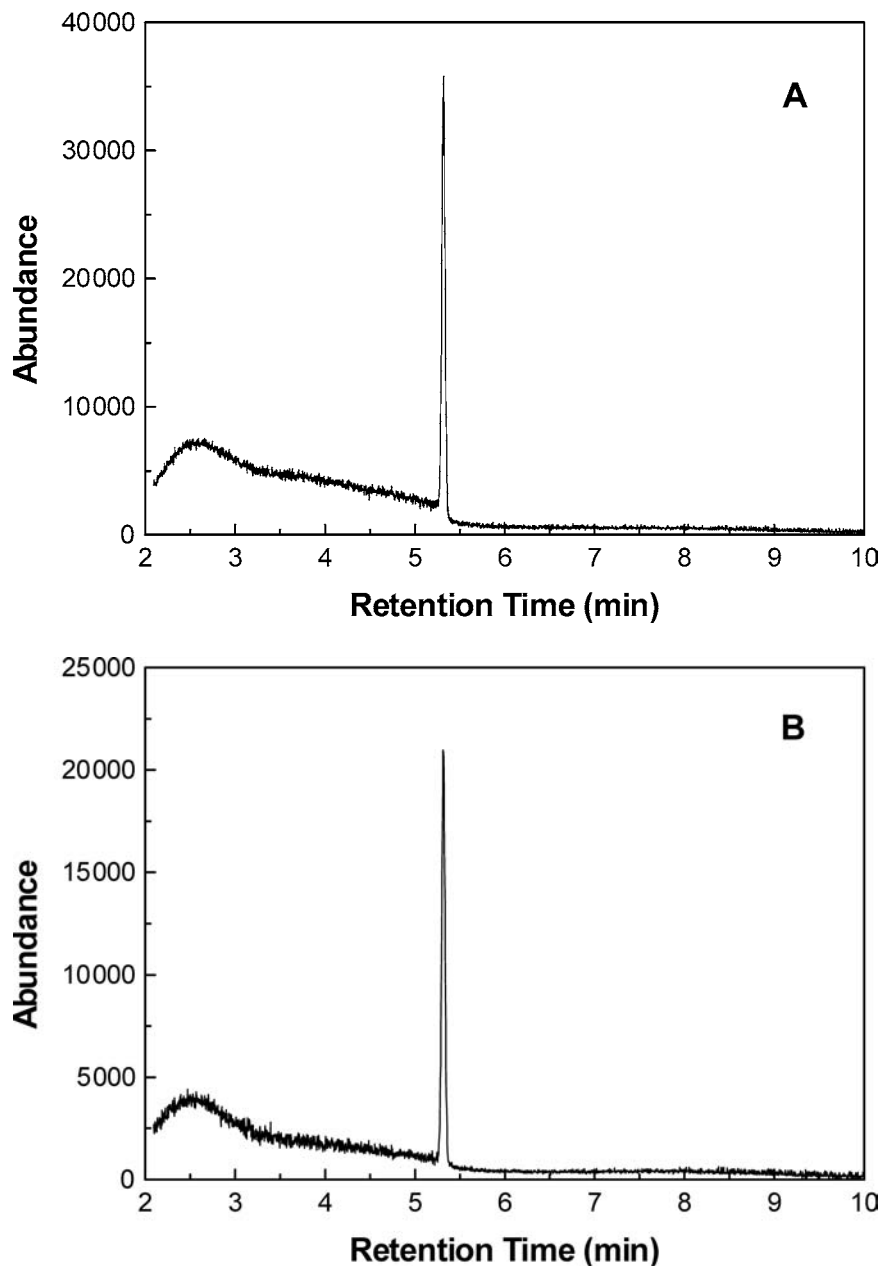


FIG. 2—(a) TIC for sample solution from  $\text{CS}_2$  extraction of unburned flash powder. (b) TIC for sample solution from  $\text{CS}_2$  extraction of unburned Pyrodex.

processed as described previously. Again, in neither case was there sufficient extracted material to perform XRD or EDX analysis. Figures 3 and 4 show the TICs and relevant fragmentation pattern for each sample. In the case of the flash powder, the elemental sulfur peak is present at a retention time of  $\sim 5.3$  min, and it is positively identified (match quality = 93). A chemical color test of the remaining extracted material from the burned flash powder confirmed the presence of elemental sulfur. In the case of Pyrodex, there is a small but distinct peak at a retention time of  $\sim 5.3$  min, superimposed upon a broad, noisy background envelope of peaks. This peak at  $\sim 5.3$  min is positively identified as elemental sulfur (match quality = 95). However, the fragmentation pattern for this peak also contains many contributions from the background envelope of peaks. When the fragmentation pattern from a point on the background just to the left or just to the right of the  $\sim 5.3$  min peak is subtracted from the fragmentation pattern of the  $\sim 5.3$  min peak, the match quality from the Wiley database search increases slightly

(from 95 to 97). The presence of elemental sulfur in the extracted material was confirmed by the chemical color test, which gave a very pale blue color.

#### 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 a 25.0 mL volumetric flask and diluting to the mark with  $\text{CS}_2$ . The resulting solution has a concentration of  $7.8 \times 10^{-4}$  M  $\text{S}_8$ , which is equivalent to 200 ng  $\text{S}_8/\mu\text{L}$  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

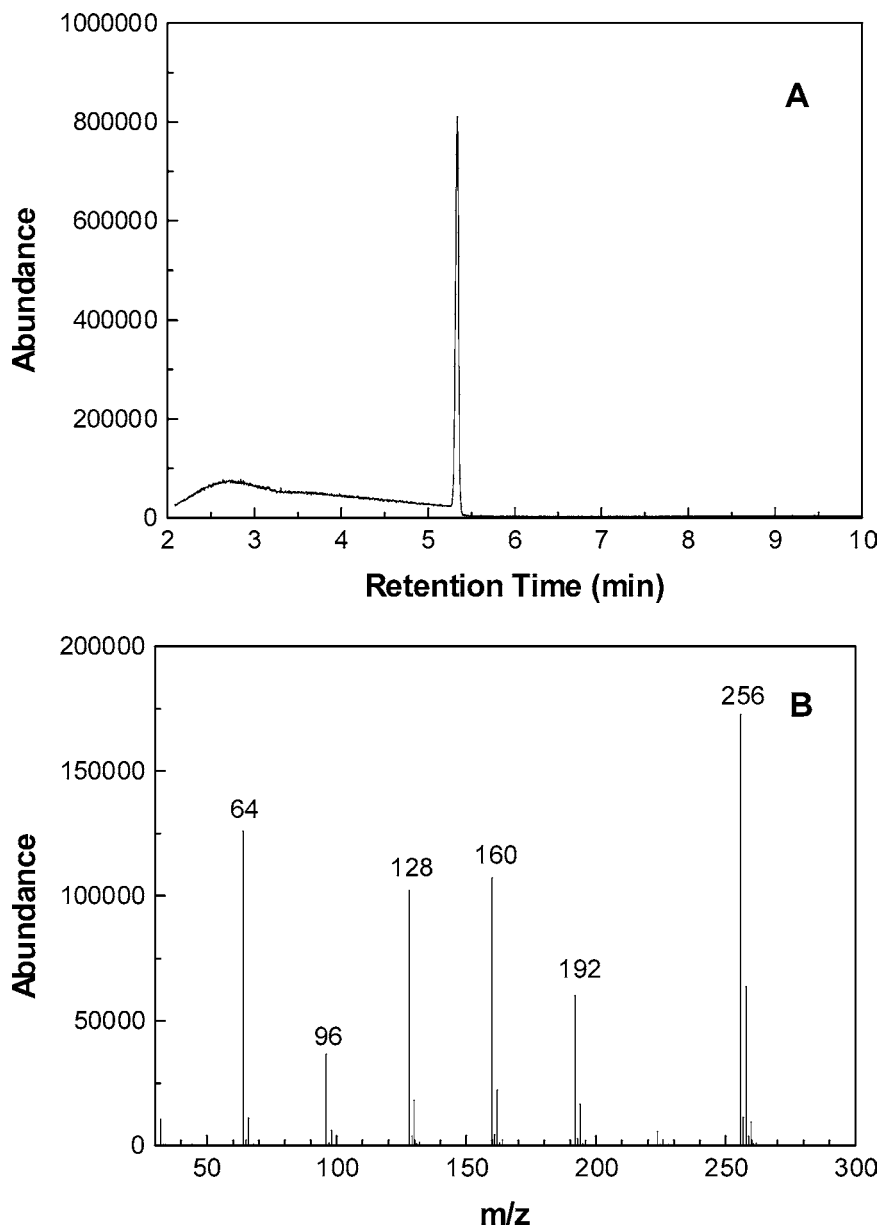


FIG. 3—(a) TIC for sample solution from  $CS_2$  extraction of burned flash powder. (b) Fragmentation pattern for peak at retention time of 5.33 min in (a).

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

Amount of $S_8$ Present	Observations
0 $\mu\text{g}$	Negative; no color
$\sim 1000$ $\mu\text{g}$	Positive; deep blue
100 $\mu\text{g}$	Positive; blue
10 $\mu\text{g}$	Positive; blue
2 $\mu\text{g}$	Positive; light blue
1 $\mu\text{g}$	Positive; very pale blue
0.8 $\mu\text{g}$	Inconclusive
0.6 $\mu\text{g}$	Inconclusive
0.4 $\mu\text{g}$	Negative; no color
0.2 $\mu\text{g}$	Negative; no color

was a known, but not quantified, sample of  $S_8$  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  $\mu\text{g}$ . Trials with 0.8  $\mu\text{g}$  and 0.6  $\mu\text{g}$  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  $\mu\text{g}$  ( $1 \times 10^{-6}$  gram).

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  $S_8$  onto the column. The resulting TICs are shown in Fig. 5. Wiley database searches were performed for the peak at  $\sim 5.3$  min in each TIC. The peaks in both the 5 ng and 2.5 ng trials were positively identifiable, with a match quality of 91 in each case, but the peak in the 1 ng trial was not positively identifiable. Thus, the detection limit for the GC-MS method for sulfur was determined to be 2.5 ng ( $2.5 \times 10^{-9}$  g), making it 400 times more sensitive for elemental sulfur than the chemical color test.

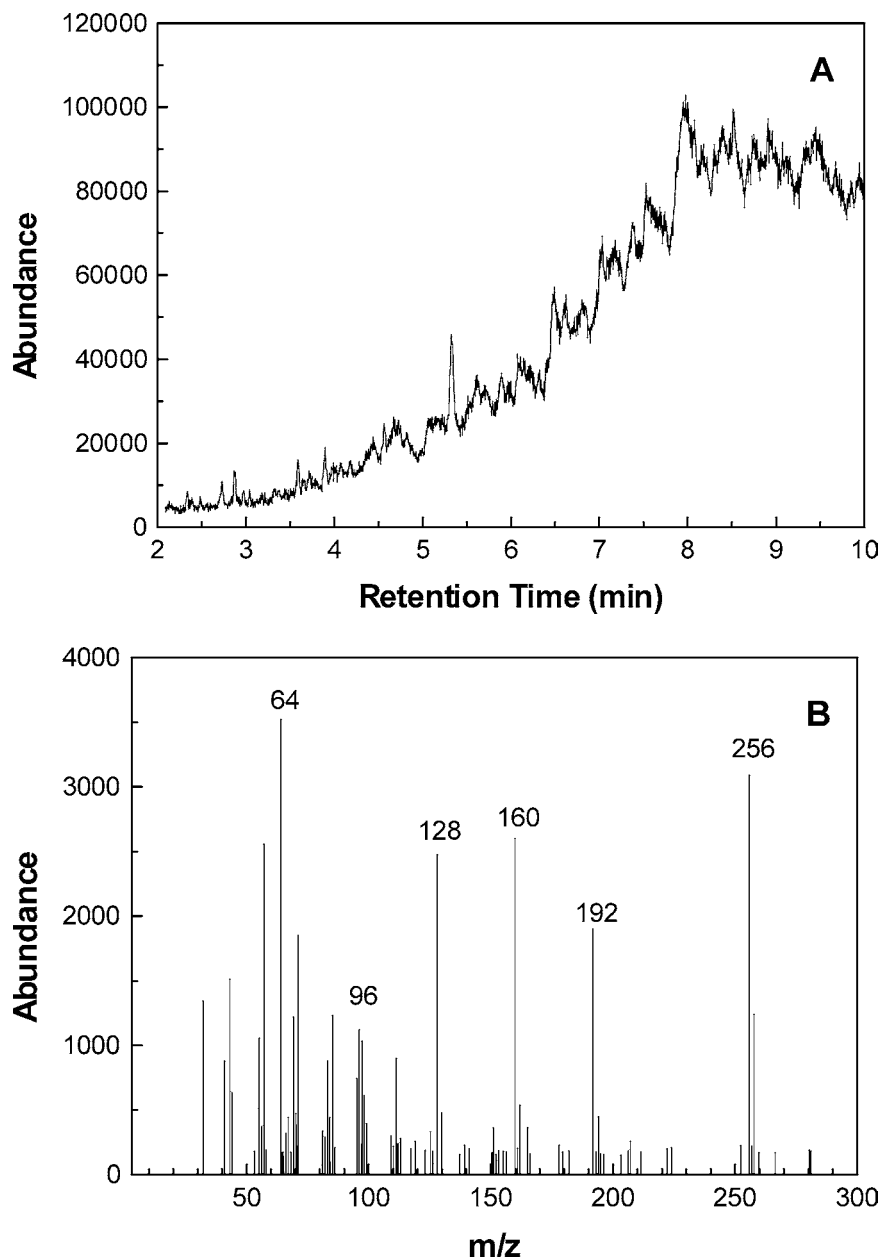


FIG. 4—(a) TIC for sample solution from  $CS_2$  extraction of burned Pyrodex. (b) Fragmentation pattern for peak at retention time of 5.32 min in (a).

The GC-MS detection limit for sulfur determined in this work is significantly higher than that of 0.096 ng reported by Chen et al. (3), who used a different column, different instrument parameters, and a longer total runtime. The 2.5 ng detection limit reported here 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. So even though the current detection limit is higher than in the previous study, it is still much more sensitive than the chemical color test, and it can be achieved in a total runtime of only 10 min.

The arson blank, described previously, provides a direct illustration of the increased sensitivity of the GC-MS method over the chemical color test. Recall that Fig. 1a shows the TIC for a 1  $\mu$ L injection of an arson blank created by eluting an activated charcoal tube with  $CS_2$ . The TIC was collected using the instrument parameters for arson analysis, with a split ratio of 40:1, and it clearly

shows a strong peak for elemental sulfur. When a 1  $\mu$ L sample of the same arson blank was placed in a clean shell vial, evaporated, and then tested using the chemical color test, there was no color change; the 1  $\mu$ L sample from the arson blank tested negative for elemental sulfur by the chemical color test. These results clearly demonstrate that the GC-MS method can detect and positively identify elemental sulfur in cases where the chemical color test cannot. Furthermore, because the split ratio was 40:1 on the GC-MS, only 1/40 of the amount of elemental sulfur in the 1  $\mu$ L injection was delivered onto the column, confirming that the GC-MS method is at least 40 times more sensitive for sulfur than is the chemical color test.

#### Reproducibility

The reproducibility of the analytical method was tested by injecting 1.0  $\mu$ L of the standard sulfur stock solution ( $7.8 \times 10^{-4}$  M  $S_8$  in  $CS_2$ ) five times. For the five trials, the peak retention time

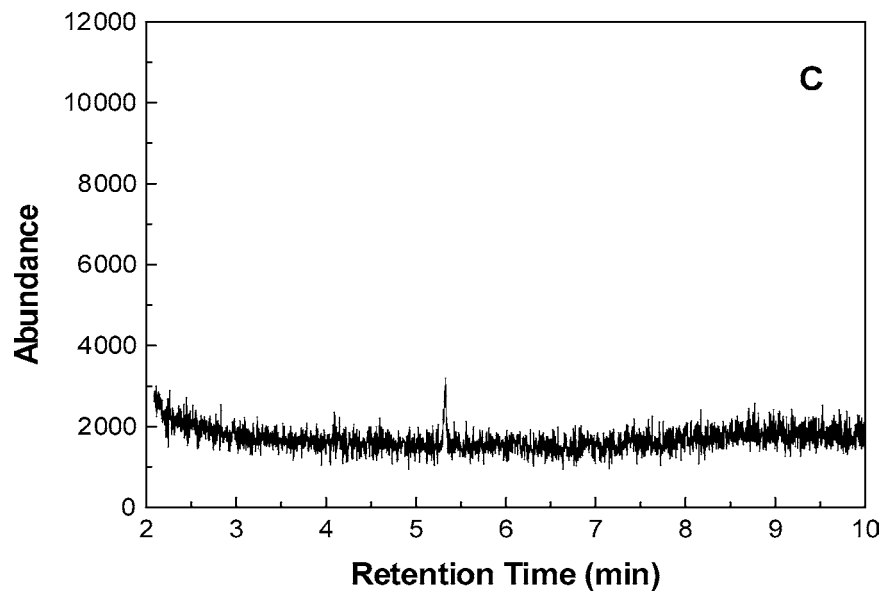
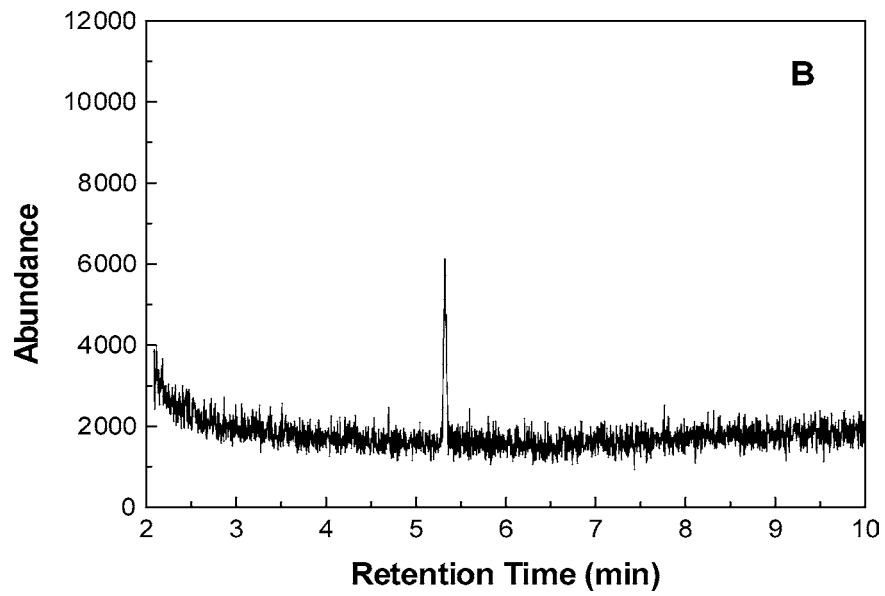
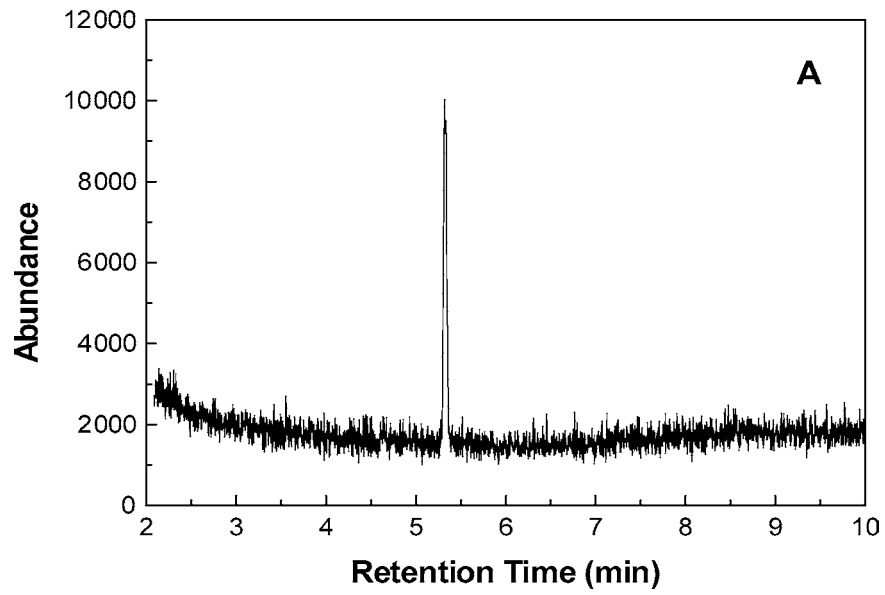


FIG. 5—TICs for (a) 5 ng, (b) 2.5 ng, and (c) 1 ng  $S_8$  on the column.

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.

Although explosives analysis 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 is 38 200 counts, and the standard deviation of the population is 3022 counts. The relative standard deviation (RSD) was found to be 8%, which is in good agreement with the results by Chen et al. (3), who achieved a RSD of 7%.

#### *Advantages and Limitations*

The 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 have interfered with the chemical color test in the past (e.g., organic dyes). Therefore, inconclusive results due to interference are minimized.
5. It can be performed using the exact same instrument and column already in use in many labs for arson analysis; therefore, in most cases, no additional equipment or instrumentation is required.
6. It does not require the preparation of any special chemical reagents.
7. It eliminates the need to use pyridine—a toxic compound with NFPA ratings as a moderate (level 2) health hazard and a severe (level 3) fire hazard—in explosives analysis.
8. TWGFEX already has declared the use of GC-MS to be sufficient for the positive identification of many organic explosives, so it is reasonable to assume that they also will accept its use for the positive identification of elemental sulfur from inorganic explosives.

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 complete case analysis for sulfur (i.e., runs for sensitivity check, blank, and sample) is 10 min, which 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<sub>2</sub> extraction of the residue, the GC-MS analysis for sulfur can 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 currently used chemical color test.

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