JOURNAL OF FORENSIC SCIENCES

J Forensic Sci, January 2011, Vol. 56, No. 1
doi: 10.1111/j.1556-4029.2010.01534.x

TECHNICAL NOTE

CRIMINALISTICS

Benjamin J. Routon,[1] B.S.; Brandon B. Kocher,[1] B.S.; and John V. Goodpaster,[1] Ph.D.

Discriminating Hodgdon Pyrodex® and Triple Seven® Using Gas Chromatography–Mass Spectrometry

ABSTRACT: Pyrodex® and Triple Seven® are black powder substitutes that often find use as fillers in improvised explosive devices, such as pipe bombs. These propellants have essentially the same overall appearance and oxidizers, but different fuels. For example, Pyrodex® contains sulfur, sodium benzoate, and dicyandiamide (DCDA), whereas Triple Seven® lacks sulfur but also contains 3-nitrobenzoic acid. In this method, intact particles and postblast solid residues were reacted with bis(trimethylsilyl)trifluoroacetamide + 1% trimethylchlorosilane in acetonitrile for 30 min at 60°C. The resultant trimethylsilyl derivatives of the organic fuels were then analyzed by gas chromatography–mass spectrometry. Each derivative was clearly resolved from other components, and high-quality mass spectra were obtained. In addition, characteristic fragments resulting from loss of a methyl radical from the molecular ion (*m/z* 163 for sulfur, *m/z* 171 for DCDA, *m/z* 179 for benzoic acid, and *m/z* 224 for nitrobenzoic acid) were able to be monitored.

KEYWORDS: forensic science, explosives, black powder substitutes, Pyrodex®, Triple Seven®, gas chromatography–mass spectrometry, sulfur, benzoic acid, dicyandiamide, nitrobenzoic acid

Pyrodex® was introduced in 1976 by the Hodgdon Powder Company (Shawnee Mission, KS) as a safer alternative to black powder for use in primitive weapons requiring propellant. It is classified by the U.S. Department of Transportation as a flammable solid and hence is much easier to store and transport than black powder. Chemically, black powder and Pyrodex® have some common components (i.e., potassium nitrate, sulfur, and charcoal). The main differences are that Pyrodex® contains less sulfur than black powder and that Pyrodex® also contains potassium perchlorate, sodium benzoate, and dicyandiamide (DCDA), in which the duo of sodium benzoate and DCDA are a unique feature of this product.

Introduced in 2001, Triple Seven® (Hodgdon Powder Company) is also a sulfur-free alternative to black powder. Pyrodex® and Triple Seven® are both similar in physical characteristics, and the particles are effectively indistinguishable (see Fig. 1). However, the two propellants can be differentiated chemically, as Triple Seven® lacks sulfur and contains 3-nitrobenzoic acid. This has led to concern regarding differentiating these two propellants in postblast residues, particularly based on their similar appearance and chemical properties, ease of availability in sporting goods/gun stores, and use in criminal weapons, such as pipe bombs.

There have been several prior works regarding the analysis and detection of intact particles of Pyrodex® and Triple Seven®. Differentiating between intact particles of these propellants is readily accomplished using techniques, such as X-ray powder diffraction (XRPD), scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS), and Fourier transform infrared spectroscopy (1). More recently, time of flight—secondary ion mass spectrometry has been utilized for this purpose as well (2). Additional techniques that can identify components of these powders in postblast residues include capillary electrophoresis (3,4), gas chromatography–mass spectrometry (GC-MS) (5), high-performance liquid chromatography (HPLC) with ultraviolet absorbance detection (6,7), and liquid chromatography–mass spectrometry (8).

A typical approach in casework is to first utilize XRPD combined with SEM-EDS to identify crystalline phases of inorganic combustion products from these and other propellants. For example, black powder deflagrates to form potassium sulfate, Pyrodex® forms potassium chloride and potassium sulfate, and Triple Seven® forms only potassium chloride (1). The methodology described here is intended for use after Pyrodex® and Triple Seven® have already been indicated via the identification of potassium chloride with or without potassium sulfate. Only then would identifying the organic fuels in these propellants be pursued to specify what black powder substitute was used.

To date, the only method that can identify all of the organic fuels (i.e., benzoic acid, nitrobenzoic acid, and DCDA) in postblast residue is the HPLC method published by Boyle and Bender (6,7). However, this method is not wholly conclusive in that it relies upon a retention time and ultraviolet absorbance spectrum to identify each organic fuel. A method for obtaining mass spectra of the components using negative ion electrospray mass spectrometry has also been presented by Dreifuss and Goodpaster (8). However, DCDA was not retained under the separation conditions used and would be susceptible to co-eluting species and suppression effects. Furthermore, sulfur was not identified in either method.

Therefore, a method is needed to identify sulfur, sodium benzoate, nitrobenzoic acid, and DCDA in postblast residues using mass spectrometry. The use of GC-MS is appealing as it is used

---

[1] Department of Chemistry and Chemical Biology, Forensic and Investigative Sciences Program, Indiana University Purdue University Indianapolis (IUPUI), Indianapolis, IN 46202-3724.

Received 29 July 2009; and in revised form 24 Oct. 2009; and accepted 7 Nov. 2009.

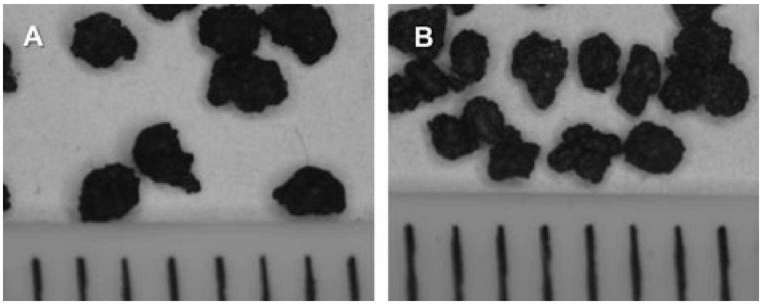

FIG. 1—*Photomicrographs of (A) Pyrodex® RS and (B) Triple Seven® RS. Scale is in mm. RS, Rifle/Shotgun.*

routinely in forensic science laboratories for the separation of complex mixtures and identification of the compounds in a sample. An inherent limitation of GC-MS is that only those compounds with appreciable volatility and thermal stability can be analyzed. For example, a GC-MS method for determining elemental sulfur in Pyrodex® and other explosives has been published, but other organic fuels were not identified (5). As a result, analysts can use derivatization agents to form more volatile products from a nonvolatile analyte. This is a well-established technique in GC-MS analysis, and derivatives have found use in identifying the organic fuels in chlorate–sugar explosive mixtures (9) and in ascorbic acid containing black powder substitutes (10).

Materials and Methods

The following chemicals were used: sublimed sulfur (Fisher Scientific, Pittsburgh, PA), DCDA (Acros Organics USA, Morris Plains, NJ), benzoic acid (Acros Organics USA), nitrobenzoic acid (Acros Organics USA), acetonitrile (Fisher Scientific), and HPLC-grade water (Fisher Scientific). The derivatization agent used was *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) as a catalyst (Pierce Biotechnology, Rockford, IL).

Samples were obtained as intact particles or from postblast debris. Intact particles *c.* 1 mg in mass were placed into 300 μL of acetonitrile, crushed with a spatula, and ultrasonicated. A volume of 300 μL of BSTFA + 1% TMCS was added, and the mixture was heated at 60°C for 30 min. The solution was then filtered and placed into a 300-μL vial insert for analysis. Postblast debris was scraped to obtain solid residue from fragments, or the fragments were extracted with water. Water extracts were prepared by repeatedly washing the fragment with 1 mL of H_2O, filtering, and then evaporating the water extract under a stream of nitrogen at 60°C. The solid residue was then derivatized as described earlier. When confirmation of sulfur in an intact sample was needed, the sample was reacted with the derivatizing reagent for 24 h prior to filtering and analysis.

GC-MS analysis was performed on an Agilent gas chromatograph (Model 6890; Agilent Technologies, Wilmington, DE) coupled with an Agilent inert mass selective detector (Model 5975) and a GERSTEL MPS 2 Liquid Injection Autosampler (GERSTEL, Inc., Linthicum, MD). Several combinations of GC-MS parameter settings were tested to determine an optimized method for DCDA, benzoic acid, nitrobenzoic acid, and sulfur analysis, resulting in the following operation settings:

Injection volume: 1.0 μL
He carrier gas-flow rate: 1 mL/min
Inlet temperature: 300°C
Split ratio: 50:1
Initial column temperature: 40°C held for 2.00 min
Initial temperature ramp: 10°C/min to 110°C
Final temperature ramp: 20°C/min to 250°C
Capillary column: 30 m × 250 μm × 0.25 μm HP-5MS
Transfer line: 250°C
MS scan mode from *m/z* 50 to *m/z* 550
Electron impact ionization with 8 min solvent delay

Postblast samples were collected after the Indiana State Police Bomb Squad initiated three improvised explosive devices in the form of pipe bombs constructed from PVC, black steel, and galvanized steel pipe bought at home improvement centers. Samples were placed in marked 1-gallon containers. Samples of Triple Seven® were also burned inside of a brown glass bottle, and the glass fragments were collected and stored in marked 1-quart containers.

Intact particles were collected from a fragment of PVC end cap and from the interior surface of glass fragments. Water extracts were obtained from locations in the end cap and around the threading of the black steel and galvanized steel pipes, as these areas yielded the greatest amount of solid residue because of partial shielding from the blast.

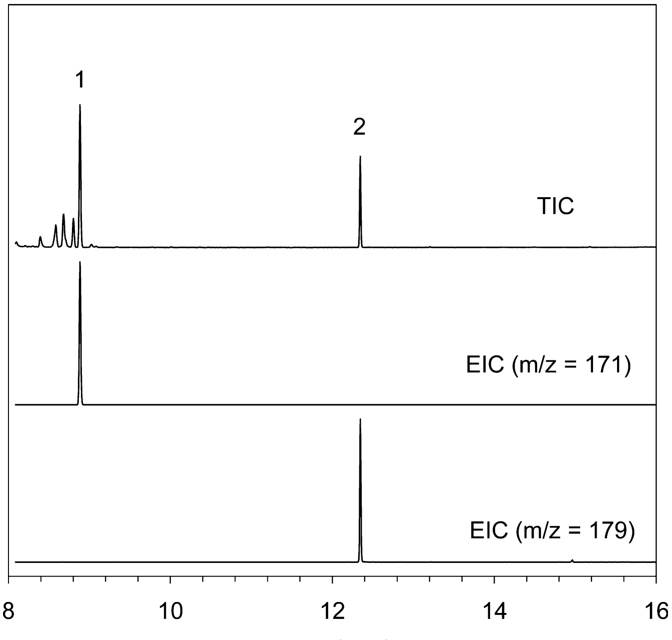

FIG. 2—*Total ion chromatogram and extracted ion chromatograms of a derivatized Pyrodex® sample. Peaks are assigned to the trimethylsilyl derivatives of (1) dicyandiamide and (2) benzoic acid.*

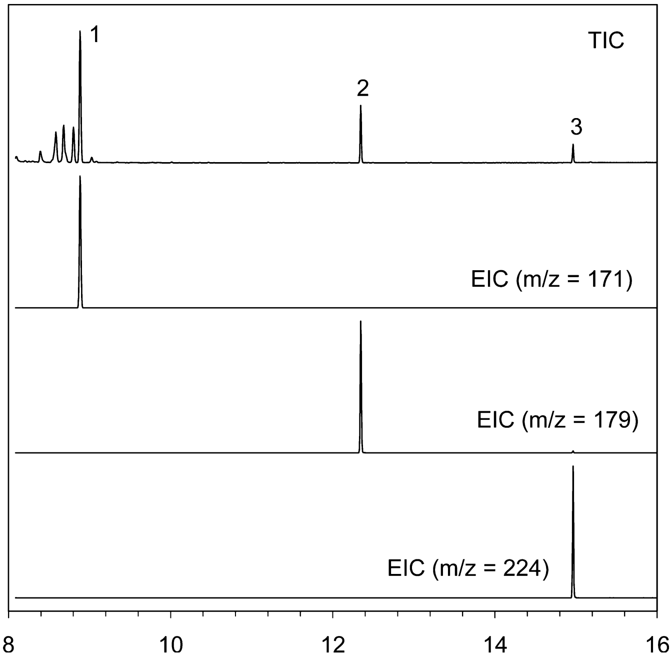

FIG. 3—*Total ion chromatogram and extracted ion chromatograms of a derivatized Triple Seven® sample. Peaks are assigned to the trimethylsilyl derivatives of (1) dicyandiamide, (2) benzoic acid, and (3) nitrobenzoic acid.*

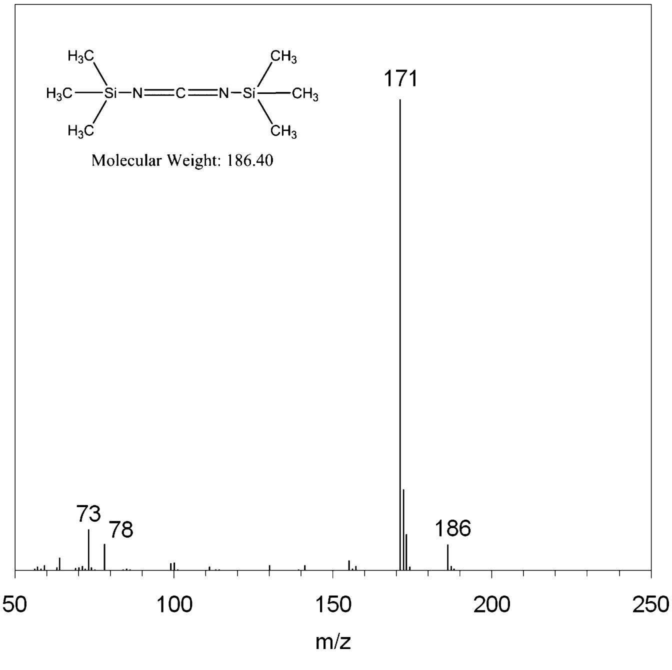

FIG. 4—*Structure and mass spectrum of the trimethylsilyl derivative of dicyandiamide.*

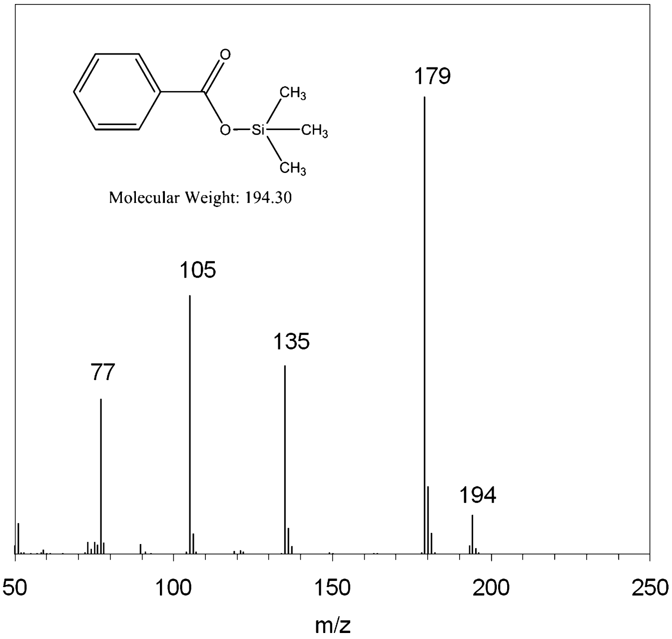

FIG. 5—*Structure and mass spectrum of the trimethylsilyl derivative of benzoic acid.*

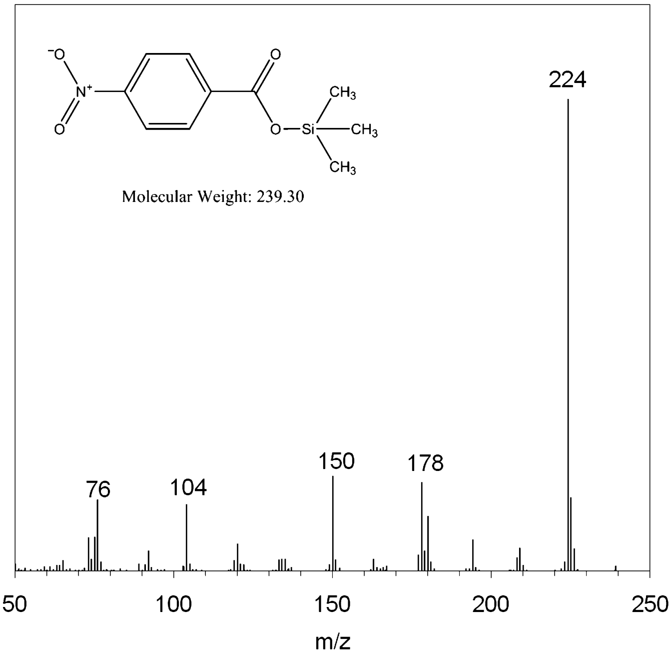

FIG. 6—*Structure and mass spectrum of the trimethylsilyl derivative of nitrobenzoic acid.*

Results and Discussion

Intact Samples

The total ion chromatogram (TIC) of a derivatized Pyrodex® sample shows two principle peaks originating from the trimethylsilyl derivatives of DCDA and benzoic acid (Fig. 2), while the TIC of a derivatized Triple Seven® sample shows an additional peak attributable to the trimethylsilyl derivative of nitrobenzoic acid (Fig. 3). The mass spectra for the derivatized fuels are shown in Figs 4–6. In each case, a characteristic peak representing the loss of a methyl radical from the molecular ion was used to construct extracted ion chromatograms (EIC) at *m/z* = 171 (DCDA), *m/z* = 179 (benzoic acid), and *m/z* = 224 (nitrobenzoic acid). The peak retention times and mass spectra were verified by forming derivatives from pure standards of each compound.

Although DCDA is somewhat sensitive to temperature, no significant degradation of DCDA was noted even though the derivatization temperature was varied from 50 to 80°C. An important aspect

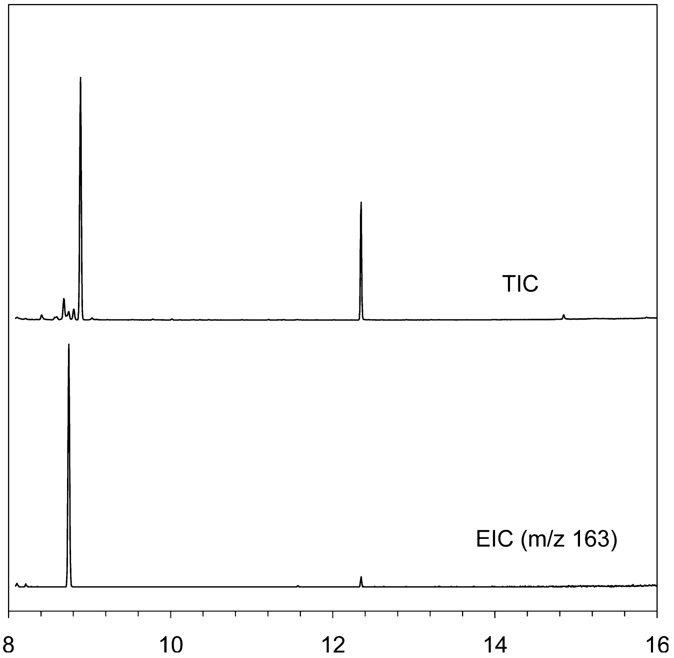

FIG. 7—*Total ion chromatogram and extracted ion chromatogram (EIC) of a derivatized Pyrodex® sample that was allowed to stand for 24 h. The peak appearing at 8.7 min in the EIC is the trimethylsilyl derivative of hydrogen sulfide.*

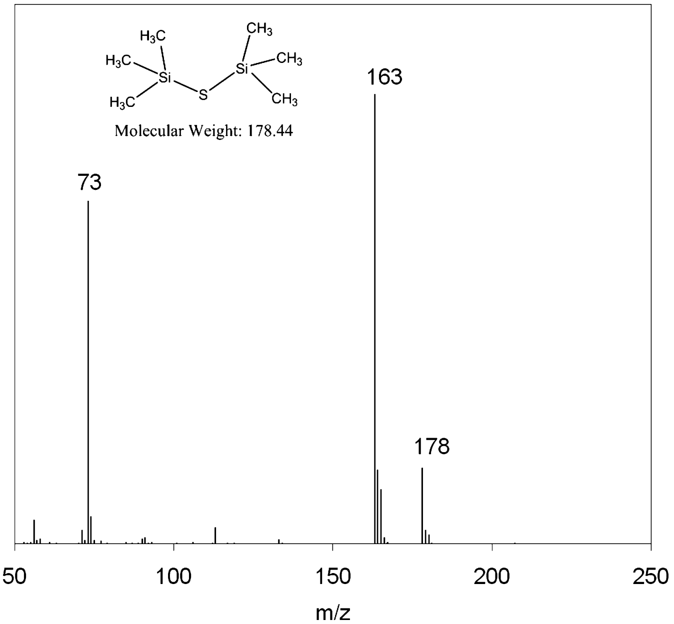

FIG. 8—*Structure and mass spectrum of the trimethylsilyl derivative of hydrogen sulfide.*

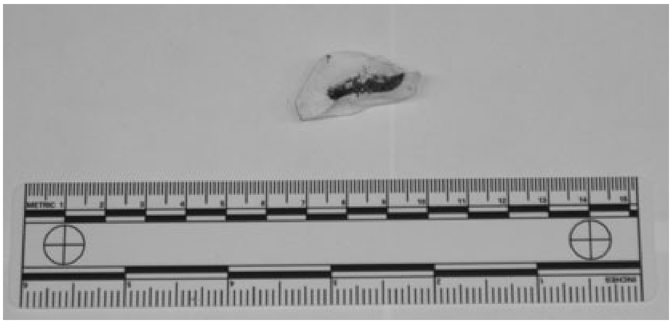

FIG. 9—*Postblast fragment from a 8-inch by 1-inch nominal diameter PVC pipe filled with Pyrodex® RS and initiated with an electric match. RS, Rifle/Shotgun.*

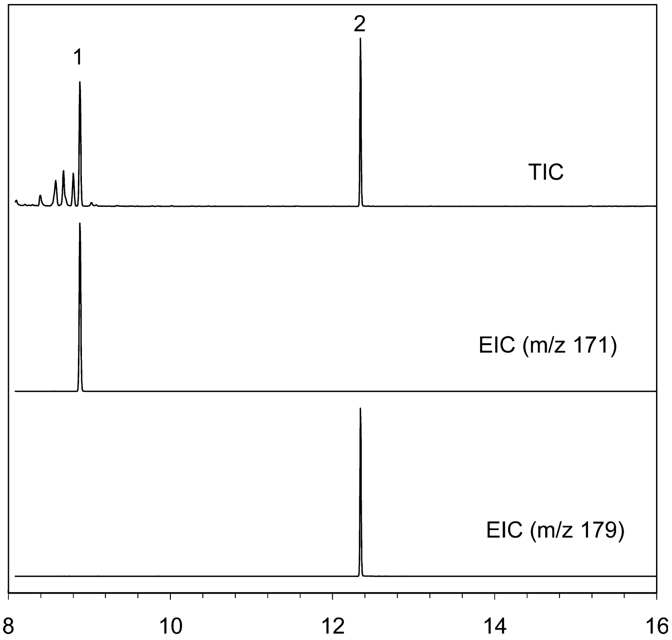

FIG. 10—*Total ion chromatogram and extracted ion chromatograms of derivatized solid residue from a PVC pipe bomb fragment. Peaks are assigned to the trimethylsilyl derivatives of (1) dicyandiamide and (2) benzoic acid.*

of the derivatization reaction for DCDA is that the derivative thus formed is that of the monomer (cyanamide). In other words, reactions of BSTFA with cyanamide (CN_2H_2) or DCDA ($C_2N_4H_4$) produce the same trimethylsilyl end product, which was confirmed by forming derivatives of the pure compounds. Therefore, if present, cyanamide will generate a false positive for DCDA. However, it is also true that cyanamide is known to dimerize in water, thus forming DCDA (11). Hence, a similar false positive reaction will occur in any method using a water extract. The extent to which cyanamide may be present in actual samples is not known, although its known uses are as a chemical precursor, agricultural additive, or alcohol-deterrent drug.

Sulfur can also be derivatized in intact samples of Pyrodex®, although the reaction is quite slow. In Pyrodex® samples that were allowed to react with BSTFA for over 24 h, hydrogen sulfide is formed and derivatized. The presence of this species in a derivatized sample of Pyrodex® is shown in Fig. 7. The hydrogen sulfide derivative was formed in reactions with pure sulfur and identified by mass spectroscopy, with a characteristic peak at *m/z* 163 as shown in Fig. 8.

Postburn and Postblast Samples

After the method had been validated with intact Pyrodex® and Triple Seven® samples, postblast samples were analyzed. The fragment(s) analyzed and the resultant chromatograms of Pyrodex® residue are shown for devices made of PVC (Figs 9 and 10) and black steel (Figs 11 and 12). In the case of the PVC fragment,

FIG. 11—*Postblast debris from an 8-inch by 1-inch nominal diameter black steel pipe filled with Pyrodex® RS and initiated with an electric match. RS, Rifle/Shotgun.*

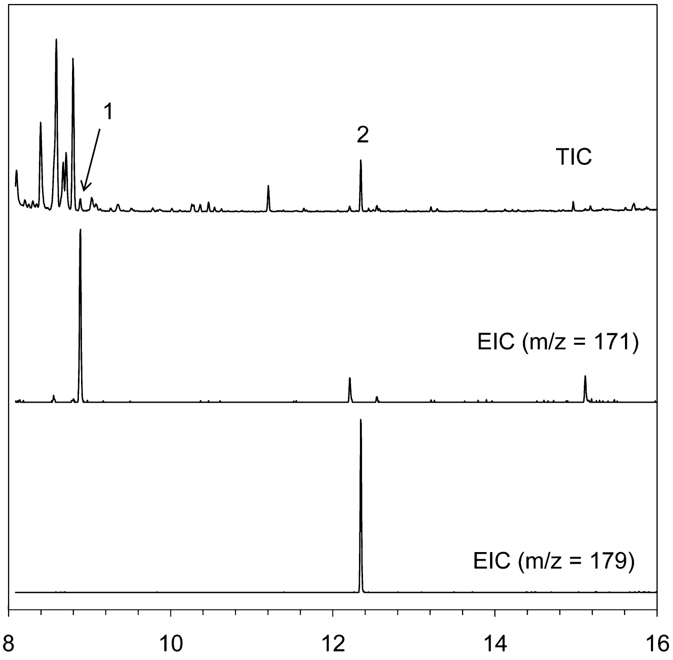

FIG. 12—*Total ion chromatogram and extracted ion chromatograms of derivatized solid residue from a black steel pipe bomb fragment. Peaks are assigned to the trimethylsilyl derivatives of (1) dicyandiamide and (2) benzoic acid.*

intact particles were located in a shielded region of the end cap, and the organic fuels are readily seen in both the TIC and the EICs. The postblast residue present on the black steel fragments required preparing a water extract, evaporating the extract, and then derivatizing the residue. In this case, the peaks are not as readily apparent, particularly in the case of the DCDA derivative. However, this peak is clear in the EIC, and an acceptable mass spectrum was obtained. Very similar results were obtained from postblast residue on galvanized steel fragments. Last, a fragment of glass from a bottle in which Triple Seven® was burned was also analyzed (Figs 13 and 14). In this case, the peak attributable to nitrobenzoic acid is quite small in the TIC, readily apparent in the EIC and identified by its mass spectrum.

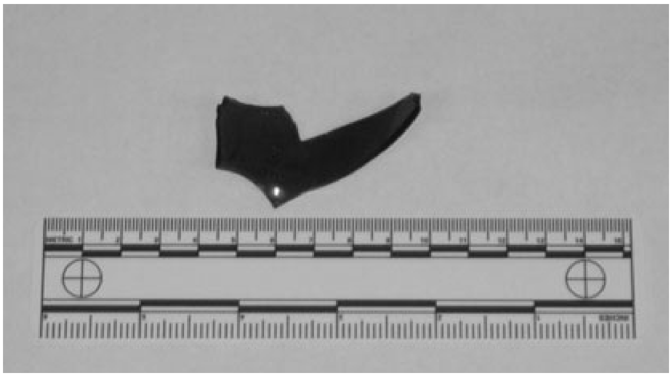

FIG. 13—*Glass fragment from a bottle in which Triple Seven® was burned.*

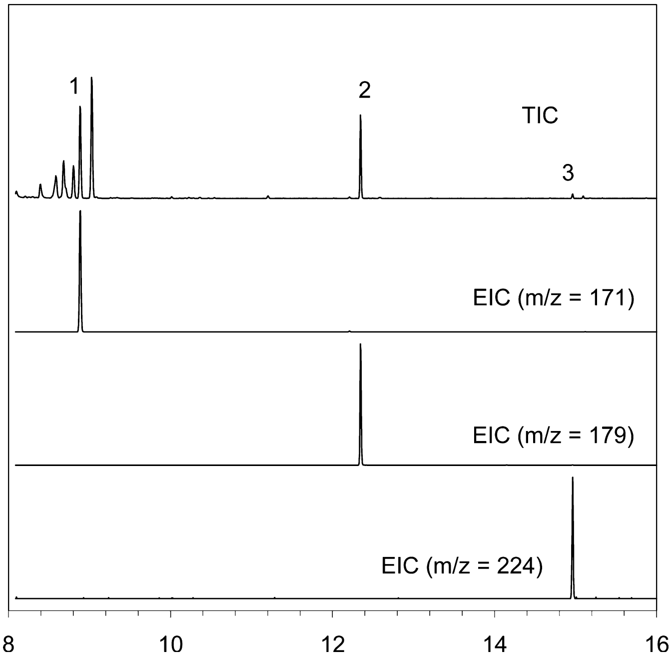

FIG. 14—*Total ion chromatogram and extracted ion chromatograms of derivatized residue from a glass fragment. Peaks are assigned to the trimethylsilyl derivatives of (1) dicyandiamide, (2) benzoic acid, and (3) nitrobenzoic acid.*

Conclusions

By forming trimethylsilyl derivatives of their organic fuels using BSTFA, the black powder substitutes Pyrodex® and Triple Seven® were clearly differentiated. This method uses commonly available instrumentation and was successful for both intact particles and postblast residue. No extensive precleaning steps were taken with the glassware used. Such procedures could be applied, if desired, to reduce background peaks.

Acknowledgments

The authors acknowledge Douglas Klapec of the ATF Forensic Science Laboratory for providing samples of Triple Seven® residue on glass. Sergeant Leonard Langland of the Indiana State Police was instrumental in coordinating and carrying out all pipe bomb explosions. Finally, JVG acknowledges Edward Bender of the ATF Forensic Science Laboratory and D.G.

Yuengling for important discussions and for providing additional samples.

References

1. Bender EC. Analysis of low explosives. In: Beveridge A, editor. Forensic investigations of explosions. Bristol, PA: Taylor & Francis, 1998;343–88.
2. Mahoney CM, Gillen G, Fahey AJ. Characterization of gunpowder samples using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Forensic Sci Int 2006;158:39–51.
3. Klapec DJ, Ng D. The use of capillary electrophoresis in the detection of monomethylamine and benzoate ions in the forensic examination of explosives residues. J Forensic Sci 2001;46(5):1168–73.
4. Hopper KG, LeClair H, McCord BR. A novel method for analysis of explosives residue by simultaneous detection of anions and cations via capillary zone electrophoresis. Talanta 2005;67:304–12.
5. Bradley KS. Determination of elemental sulfur in explosives and explosive residues by gas chromatography-mass spectrometry. J Forensic Sci 2005;50(1):1–8.
6. Bender EC. The analysis of dicyandiamide and sodium benzoate in pyrodex by HPLC. Crime Lab Dig 1989;16:76–7.
7. Boyle KM, Bender EC, editors. The analysis of the hodgdon powder company's black powder substitutes. The 8th International Symposium on the Analysis and Detection of Explosives; 2004 June 6–10; Ottawa, Canada. Ottawa, Canada: RCMP Forensic Laboratory Services/RCMP Public and Emergency Preparedness, 2004.
8. Dreifuss PA, Goodpaster JV, editors. Atmospheric pressure ionization LC/MS methods for the analysis of black powder substitutes. The 8th International Symposium on the Analysis and Detection of Explosives; 2004 June 6–10; Ottawa, Canada. Ottawa, Canada: RCMP Forensic Laboratory Services/RCMP Public and Emergency Preparedness, 2004.
9. Nowicki J, Pauling S. Identification of sugars in explosive residues by gas chromatography-mass spectrometry. J Forensic Sci 1988;33(5): 1254–61.
10. Goodpaster JV, Keto RO. Identification of ascorbic acid and its degradation products in black powder substitutes. J Forensic Sci 2004;49(3): 523–8.
11. Turowski M, Deshmukh B. Direct chromatographic method for determination of hydrogen cyanamide and dicyandiamide in aqueous solutions. Anal Lett 2004;37(9):1981–9.

Additional information and reprint requests:
John V. Goodpaster, Ph.D.
Indiana University Purdue University Indianapolis
Forensic and Investigative Sciences
402 North Blackford Street LD 326
Indianapolis, IN 46202
E-mail: jvgoodpa@iupui.edu