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Technical Note

Mapping smokeless powder residue on PVC pipe bomb fragments using total vaporization solid phase microextraction

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ABSTRACT

Quantitating post-blast explosive residue is not a common practice in crime labs as it is typically not legally relevant. There is value in quantitation, however, if the distribution of residues on Improvised Explosive Devices (IEDs) can help guide future sample collection and/or method development. Total vaporization solid phase microextraction gas chromatography mass spectrometry (TV-SPME/GC/MS) was used to quantify residues of double-base smokeless powder (DBSP), which includes nitroglycerin (NG), diphenylamine (DPA), and ethyl centralite (EC) on post-blast PVC pipe bomb fragments. The analytical method could separate the three constituents in under 5 min with a detection limit under 1 ppb, which demonstrates high throughput while maintaining high sensitivity. The method was optimized for nitroglycerin, as it is the most indicative of DBSP. The average mass of nitroglycerin recovered from an entire PVC device was 1.0 mg. The average mass of diphenylamine recovered was much lower (24 μg) and only one device had detectable levels of EC. The typical concentration of NG on any given fragment was approximately 15–30 ppm (μg NG/g fragment). However, there was no correlation between the mass of a fragment and the mass of residue upon it. Instead, the residue was distributed such that the highest concentration of residues was found on end cap fragments.

Although it is not commonly known among the public, criminal bombings occur almost daily in the United States. For example, over 36,000 illegal bombing incidents occurred in the United States between 1983 and 2002 leading to over 5900 injuries and 699 deaths [1]. The most recent statistics from the U.S. Bomb Data Center show that the number of explosive incidents reported in the U.S. has been steadily increasing since 2009. Although the number of people that were injured and killed declined between 2004 and 2007, a large increase is seen in 2013 due to the Boston Marathon Bombing (Fig. 1).

Among the various types of Improvised Explosive Devices (IEDs), pipe bombs are easily constructed from readily available materials. Materials such as pipes and endcaps are found in hardware stores, and low explosives are available at sporting goods stores. For example, double base smokeless powder (DBSP) is a deflagrating low explosive that will cause an explosion if contained. In addition to nitrocellulose, DBSP contains the energetic compound nitroglycerin (NG), as well as stabilizers and plasticizers such as diphenylamine (DPA) and ethyl centralite (EC).

Traditionally, analysis of post-blast pipe bomb fragments is limited to qualitative identification of the explosive as the legal issue is what, not how much of an explosive is present [2]. However, there is value to quantitation in explosives research, as it provides information on how devices explode, the amount of explosive residue remaining for analysis, as well as what instrumental sensitivity is required for analysis. Additionally, mapping of the residue may shed light on which type of fragments tend to have the highest concentration of residues.

Trace analysis of high explosives in complex matrices using absorptive/adsorptive media is an established practice and is routinely applied to explosives investigations. For example, nitroaromatic explosives have been extracted from aqueous samples using a molecularly imprinted silica sorbent and analyzed using liquid chromatography [3]. Direct immersion solid phase microextraction (SPME) coupled with gas chromatography with electron capture detection was utilized to identify and quantitate 2,6-dinitrotoluene, trinitrotoluene, and pentaerythritol tetranitrate from aqueous solutions [4]. Additionally, triacetone triperoxide (TATP) residue from various witness materials was analyzed

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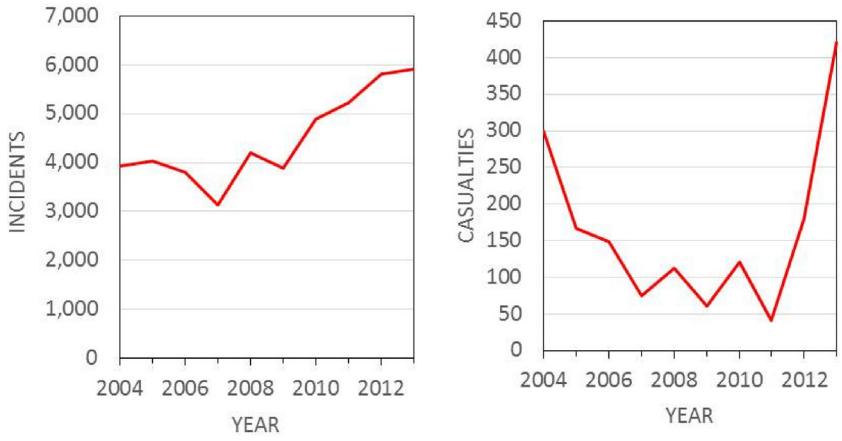

Fig. 1. Bombing incidents and casualties from 2004 to 2013.

using headspace SPME with gas chromatography mass spectrometry [5].

There are also many analytical techniques that can be used to detect constituents of smokeless powder, a common filler in pipe bombs. These techniques include liquid chromatography mass spectrometry [6], gas chromatography coupled with thermal energy analysis as well as mass spectrometry [7], and capillary zone electrophoresis [8,9]. The National Center for Forensic Science's Smokeless Powder Database lists standard operating procedures and instrumental methods for the analysis of smokeless powder. Additionally, the Technical Working Group for Fire and Explosions Analysis (TWGFEX) released a guide in 2009 for the forensic identification of post-blast residues using categorized analytical techniques [10].

Our research group has a long-standing interest in simple IEDs such as pipe bombs. This includes studies of pipe bomb explosions using high speed videography [11,12], chemical analysis of post-blast residues on pipe bomb fragments [13], and quantitation of explosive residues on witness plates placed immediately adjacent to a pipe bomb [14]. The technique that has been used for all of these studies is Total Vaporization Solid Phase Microextraction Gas Chromatography/Mass Spectrometry (TV-SPME/GC/MS) [15]. In this method, a solvent extract is completely vaporized inside a headspace vial and the vapor is then sampled using SPME. As TV-SPME completely vaporizes the liquid extract, an equilibrium is established between the vapor phase analyte and the SPME fiber coating. In comparison to liquid injection of organic extracts, TV-SPME increases the sensitivity by an order of magnitude, allowing lower concentrations and larger sample volumes to be analyzed.

Prior work on fragments from steel pipe bombs determined that the total mass of NG recovered from the remains of an eight inch steel device ranged from 0.47 to 2.2 mg, with concentrations on individual fragments ranging from 51.1 to 3.0 ppm (μg/g) [13]. In contrast, the concentration of DPA and EC were 1–2 orders of magnitude lower [13]. The distribution of residues in steel deices was clearly not homogenous in that fragments from the end caps of the devices had residue concentrations that were 10–100 times higher than fragments from the pipe body.

In a similar study, DBSP residues were quantitated on witness plates suspended immediately adjacent to PVC pipe bombs [14]. The concentration of NG was extremely varied, with essentially no NG detected on the witness plate that was facing the fused end of the device. In contrast, the four witness plates that faced the pipe body (top, bottom, right and left) all collected substantial amounts of residue. The pipe body corresponds to the location where PVC devices first begin to fail [11,12].

This paper focusses on PVC pipe bomb fragments, which have yet to be studied. As was done previously, the amount and distribution of explosive residues on PVC pipe bombs was determined by TV-SPME/GC/MS. PVC devices are known to fail much more slowly and fragment more extensively than steel devices. In addition, and unlike steel devices, PVC devices first fail along the pipe body as both the end caps are cemented to the pipe body which has similar strength. Therefore, our working hypothesis was that the amount and distribution of explosive residues on PVC would necessarily differ from steel.

1. Materials and methods

1.1. Materials

PVC pipe (8″ × 1″ diameter) and PVC endcaps (1″ diameter) were purchased at Home Depot, and Alliant Red Dot double base smokeless powder was obtained from Gander Mountain in Indianapolis, IN. SPME vials and PTFE caps were acquired from Gerstel. Polyethylene glycol SPME fibers, ethyl centralite (99%), and acetone were obtained from Sigma Aldrich. Standards of nitroglycerin (1 mg/mL) and diphenylamine (ACS grade) were purchased from Restek and Acros Organics respectively.

1.2. Pipe bomb construction and initiation

The constructed pipe with endcaps were divided into three sections:

1. Left endcap (1.8 in length × 1.2 in diameter) and one third of the pipe body (1.2 in diameter × 2.67 in length). When assembled, these sections had an internal surface area of approximately 11.2 in.^{2}.
2. Middle section of the pipe body (1.2 in diameter × 2.67 in length). These sections had an internal surface area of approximately 10 in.^{2}.
3. Right endcap (1.8 in length × 1.2 in diameter) and one third of the pipe body (1.2 in diameter × 2.67 in length). When assembled, these sections had an internal surface area of approximately 11.2 in.^{2}.

Each section was color coded with white, black, or orange paint. Only three color zones were used in this study due to the high fragmentation that was anticipated, the tendency of PVC end caps to remain adhered to the pipe body post-blast and the difficulty of differentiating end cap fragments from pipe body fragments. Determining the distribution of residues in a higher "resolution"