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Characterization of residual gunpowder recovered from articles of clothing utilizing thermal desorption GC/MS

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Introduction

Gunshot residue (GSR) is the collective name of the complex mixture of organic and inorganic particles originating from the firearm, the firearm ammunition and the combustion products, which are produced during the discharge of a firearm. Organic compounds mainly originate from propellant powders, firearm lubricants, some products of their transformation and hydrocarbons.[1] Current testing methods primarily employ the use of scanning electron microscopy, which places the lead focus on inorganic components. Utilizing Gas Chromatography/Mass Spectrometry to identify unknown organic compounds creates a powerful tool in the forensics market, specifically GSR. Using thermal desorption (figure 1) to extract residue constituents form articles of clothing could prove to be an effective technique in analyzing GSR for forensic analysis. Thermal desorption was used to replace the standard solvent extraction methods. The thermal desorption method recovered more stabilizers and accelerants than the original solvent method.

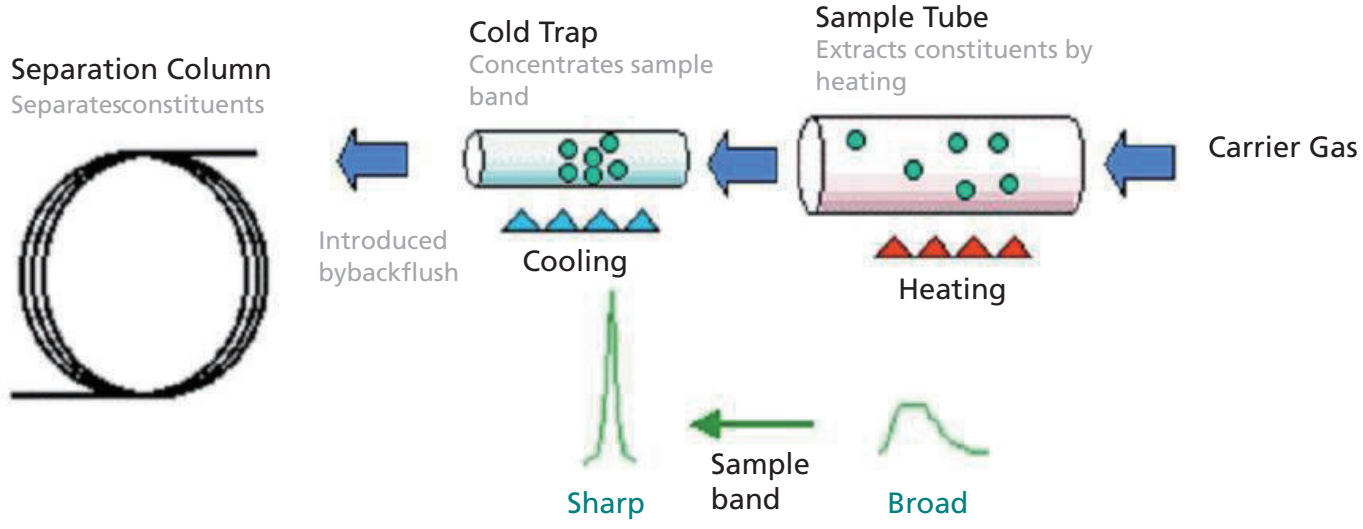

Figure 1: Schematic of thermal desorption technique

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Numerous studies have been performed analyzing GSR. A comprehensive list has been created over time compiling the commonly found organic residues.[2] The following list combines multiple studies into an consensus list of GSR related targets (shown in Table1).

Table 1: Comprehensive list of organic GSR components

1,2,3-Trimethylbenzene	2-Furaldehyde	Carbanilide	Methyl cellulose
1,2,4-Trimethylbenzene	2-Naphthol	Carbazole	Methyl centralite (MC)
1,3,5-Trimethylbenzene	2-Nitrobenzene	Charcoal	Monomethyl-phthalate
1,3,5-Trinitrobenzene	3-Nitrobenzene	Chrysene	Naphthalene
1,3-Dinitrobenzene	4-Nitrobenzene	m-Cresol	N,N-diphenylformaide
1,2-Dicyanobenzene	2-Nitrophenylamine (2-NDPA)	o-Cresol	Nitrocellulose (NC)
1,3-Dicyanobenzene	4-Nitrodiphenylamine (4-NDPA)	p-Cresol	Nitroglycerin (NG)
1,4-Dicyanobenzene	2-Nitrotoluene	Cyclonite (RDX)	Nitroguanidine
1,2-Dinitroglycerin	3-Nitrotoluene	Dextrin	N-nitrosodiphylamine (N-NDPA)
1,4-Dimethylnaphthalene	3,5-Dinitroaniline	Diazodinitrophenol	Octogen (HMX)
2,6-Dimethylnaphthalene	4-Methylbiphenyl	Diazonitrophenol	Pentaerythritol tetranitrate (PETN)
1-Methyl-3,3-diphenylurea	4-Nitrosodiphenylamine	Dibutylphthalate (DBP)	Phenanthrene
1-Methylnaphthalene	Acenaphthene	Diethylene glycol	Phenol
2-Methylnaphthalene	Acenaphthylene	dinitrate	Phytane
2-Naphthalenecarbonitrile	Akardite I (AKI)	Dimethylphthalate (DMP)	Pyrene
2,2′-Dinitrodiphenylamine	Akardite II (AKII)	Dimethylsebacate	Quinoline
2,4′-Dinitrodiphenylamine	Akardite III (AKIII)	Dinitrocresol	Resorcinol
4,4′-Dinitrodiphenylamine	Aniline	Dinitro-ortho-cresol	Rubber cement
2,3-Dimetyl-2,3-dinitrobutane	Anthracene	Diphenylamine (DPA)	Sodium alginate
2,3-Dinitrotoluene (2,3-DNT)	Benzaldehyde	Ethyl centralite (EC)	Starch
2,4-Dinitrotoluene (2,4-DNT)	Benzene	Ethylbenzene	Styrene
2,6-Dinitrotoluene (2,6-DNT)	Benzo[a]pyrene	Ethylene glycol dinitrate	Tetracene
2,4,6-Trinitrotoluene (TNT)	Benzonitrile	Fluoranthene	Toluene
2,4-Dinitroanisole (DNAN)	Benzophenone	Fluorene	m-Tolunitrile
2,4-Dinitrodiphenylamine	Benzothiazole	Gum arabic	o-Tolunitrile
4,4-Dinitrodiphenylamine	Benzylnitrile	Gum tragacanth	p-Tolunitrile
4-Amine-2,6-dinitrotoluene	Biphenylene	Indene	Urethane
2-Ethyl-1-hexanol	Butylcentralite (BC)	Indole	m-Xylene
2-Ethylhexanal	Butylphthalate	Isoquinoline	o-Xylene
2-Ethylnaphthalene	Camphor	Karaya gum	p-Xylene

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Experimental

A single vendor of 9mm ammunition was used to keep consistency throughout the analysis. Before thermally desorbing the gunpowder powder residue, it was first placed in a saturated methanol solution. One microliter was injected onto a standard Tenax TD tube; the tube was then desorbed at a temperature of 250 °C onto the trap, which was set at -20 °C. Full scan data was acquired of a mass range of 50m/z – 500m/z. Qualitative analysis was performed on the sample to identify the unknown components. The purpose of running the gunpowder in methanol was to characterize the already present compounds before combustion. Using the same brand of ammunition, a fired shell was then analyzed. The combusted cartridge was swabbed with a Qtip and then soaked in methanol solution in order to remove any left over components from the Qtip. One micro liter of the solution was injected on to a Tenax TD tube and run under the same conditions. Finally, the article of clothing worn during the time of combustion was sampled. A Qtip was used to swab the central chest area of the clothing, as well as the end of sleeve area. Similar to the previous sample, the Qtip was soaked in methanol. One microliter of the solution was injected onto a Tenax TD tube.

Table 2: Instrument Acquisition Parameters

Thermal Desorption	TD-30
Tube Material	Tenax
Tube Desorb	250°C
	60mL/min for 5min
Trap Cooling temp	minus 20°C
Trap Desorb	250°C
Joint	250°C
Valve	250°C
Transfer Line	250°C
Gas Chromatogram	GC-2010 Plus
Injection	20:1 Split ratio
Column	Rxi-5 MS 30m x 0.25mm x 0.25µm
	Helium carrier gas
	Constant linear velocity 43.4
	Column Flow 1.44
	Purge Flow 3.0 mL/min
Oven Program	40°C hold for 2.0 min
	20°C/min to 300°C, hold 3.0 min
	10°C/min to 210°C
	Total GC run time 27.0 min
Detector	GCMS QP 2010Ultra
Operating mode	Scan, EI mode, 70eV
Ion source	200°C
Interface Temp	250°C
Solvent cut time	0.5
Start Time - End time	1.0 - 18.0
Mass Range	30 - 400

Results

Figure 2 shows the chromatograms for the Gunpowder saturated in methanol. The main components were identified and compared from sample to sample.

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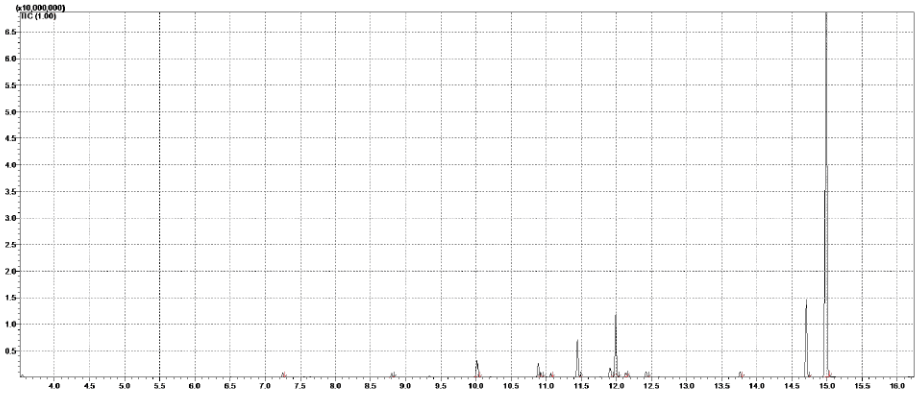

Figure 2: TIC of gunpowder in MeOH

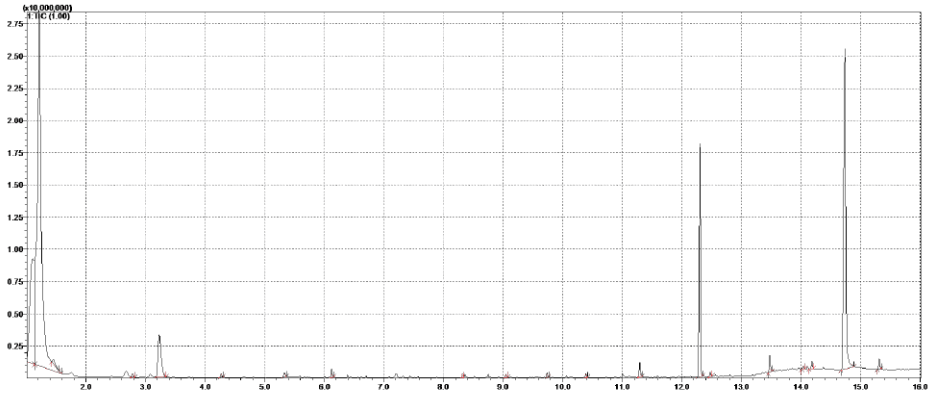

Figure 2: TIC residual GSR recovered from 9mm casing

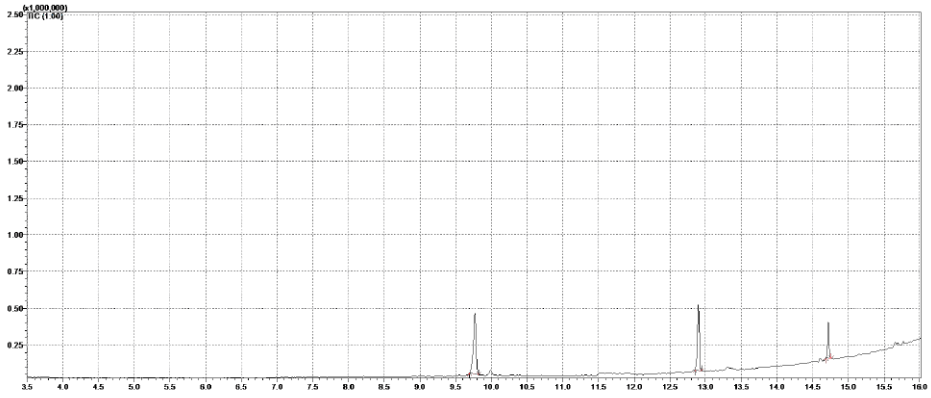

Figure 2: TIC residual GSR from article of clothing

A list of the major OGSR residue compounds that were found in the casing sample and clothing was compiled to compare area counts. Not all compounds were selected, only the major components that we expected to see. The table with the components and their respective area counts can be seen below. Library search was performed using NIST 17.

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Table 3: List of major organic components found in Gunshot Residue

Compound Name	Casing (Area cout)	Clothing (Area Count)
Glycine	213528	59208
Trimethyl Benzene	215529	70287
2-furaldehyde	198217	82927
Benzaldehyde	207572	104678
2-Pyrrolidinone, 1-methyl-	230327	19389
Nitroglycerin	3474882	168932
Carbazole	3818891	117843

Summary and Conclusions

The difference between the saturated gun powder and the casing was large, but to be expected. Different byproducts were formed after the process of combustion. Listed above in table 3 are the compounds recovered in the casing sample. This is not to say that these are the most influential markers, but that they are the compounds recovered from the casing sample. These compounds were compared to the article of clothing that was swabbed in hopes of seeing the same residual components. In fact, the compounds were detected, but in much lower amounts. There are many factors that might have had an effect on the results. The time at which the clothing was sampled is the primary explanation. Most of these compounds may have been lost before sampling occurred. The second potential reason could be the swabbing technique. Even though the recoveries were low, there is promise in this new form of sampling for GSR, which could become a powerful tool in the forensics market.

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