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TECHNICAL NOTE

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A Novel Method for the Analysis of Discharged Smokeless Powder Residues

ABSTRACT: A novel method for the estimation of intermediate-long firing distance range is proposed. The method is based on the characterization and chemical analysis of the smokeless powder particles on the target. An adhesive lifter is applied to collect the suspected gunshot residues (GSRs) from the surface of an object, and a Modified Griess Test (MGT) is carried out after alkaline hydrolysis on the adhesive lifter. Visualized particles are removed from the adhesive lifter under a microscope. Two systems are used for the analysis of organic discharge residues from the smokeless powder: (1) gas chromatography/thermal energy analysis (GC/TEA) for the analysis of nitroglycerine (NG) and 2,4-dinitrotoluene (2,4-DNT), (2) gas chromatography/mass spectrometry (GC/MS) for the identification of organic components such as DNT, NG, and some stabilizers. By using this procedure and confirming that the suspected particles are indeed GSR, one can estimate the intermediate-long firing distance of *c*. 0.75–3 m in the presence of very few particles and provide information for the classification of ammunition type in casework.

KEYWORDS: forensic science, smokeless powder, gunpowder residues, gas chromatography-mass spectrometry, gas chromatography-thermal energy analyzer, firing distance

Firing distance estimation is based on the appearance of the bullet entrance hole and the examination of gunshot residue (GSR) patterns around the hole using various techniques (1). The GSR around the bullet entrance hole can be detected visually or microscopically if the target is light enough. Smokeless powder particles can be identified by their size, shape, and color. They are regularly shaped like disks, balls, or tubes with a graphite gray-black color. On firing, most of the particles lose their gray-black color and become greenish-yellow. In most cases, color chemical tests are needed to assess the GSR pattern around the bullet entrance hole.

Modern gunpowder is mainly composed of nitrocellulose (NC). Other explosive ingredients like nitroglycerine (NG) and stabilizers such as diphenylamine (DPA), ethyl centralite (EC), methyl centralite (MC), hydroquinone, or resorcinol, and flash suppressors such as 2,4-dinitrotoluene (2,4-DNT) are also usually present. Plasticizers such as dibutylphthalate (DBP) and some reaction products of the stabilizers like 2-nitrodiphenylamine (2-NDPA) and 4-NDPA can also be present, in small quantities. Numerous studies have been published on the analysis of GSR by various analytical methods (2–12).

The routine method for firing distance estimation on clothing items in our laboratory has been described in a previous paper (13). The main steps of the method are:

(1) Transfer of the smokeless powder residues from the target to an adhesive lifter, 25 × 25 cm.
(2) Visualization of lead and copper deposits on the target itself by the rhodizonate and the rubeanic acid tests.
(3) Hydrolysis of the smokeless powder residues that have been transferred to the adhesive lifter.
(4) Modified Griess Test (MGT) for visualization of total nitrite from gunpowder on the adhesive lifter.

At close distances when many smokeless powder particles are present around the entrance bullet hole, a typical pattern is formed by the MGT and the shooting distance can easily be estimated (13). The MGT visualization is a simple microchemical test. The microtrace smokeless powder particles test can take place even in the presence of complex matrices such as soil, blood, sweat, etc. No cleanup of the sampled particles is needed before the analysis. As the distance between the gun muzzle and the target surface is increased, the GSR pattern becomes wider and the amount of smokeless powder deposition decreases (1).

At intermediate-long distances, between 0.75 and 3 m depending on the ammunition and the weapon type used, very few GSR particles usually deposit on the target. In such a case, MGT will develop only a few color spots by reaction with nitrite groups. A few spots do not form a distinct pattern. The interpretation of their origin to be only from GSR becomes problematic as they may be due to inorganic nitrite unrelated to GSR or NC found in other sources such as lacquers, varnishes, and celluloid films (2). Inorganic nitrite or nitrites that are obtained from hydrolysis can react with the MGT so it cannot be stated definitively that these few particles are indeed smokeless powder residues.

For estimation of the intermediate-long firing distance, it is first necessary to verify that the source of the color spots is from smokeless powder residues. A novel method for the analysis and

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identification of the organic propellant residues from the clothing covering the target/victim is proposed.

Experimental

Ammunition, Shooting, and Sampling

Firing was carried out in an indoor shooting range, using a 9 mm parabellum FN semiautomatic pistol. Four types of ammunition were used, all of them full metal jacket: TZZ (Israel Military Industry, Israel), GFL (Fiocci, Italy), Winchester Super X (Olin Corp.), and CCI Blazer (Cascade Cartridge Co.).

The smokeless powder particles were sampled in three steps:

(1) Preshot: the cartridge was opened and four gunpowder particles were removed, and then the cartridge was reloaded. Three particles were examined by GC/MS and one particle by GC/TEA.
(2) Postshot untreated: the reloaded cartridge was fired at a cotton cloth target from a distance of 0.5 m. The cloth target was sampled directly for gunpowder particles. Three particles were examined by GC/MS and one particle by GC/TEA.
(3) Postshot treated: particles were sampled using an adhesive lifter, hydrolyzed with alcoholic KOH, and treated with MGT. For each type of ammunition, four particles were recovered from the adhesive lifter for further analysis. Three particles were examined by GC/MS and one particle by GC/TEA.

Total Nitrite Pattern Visualization

Materials

(1) A peelable (low adhesion) transparent adhesive lifter ("JAC Vinyl," 80 μm, 25 × 25 cm) with a protective cover (supplied by ISA Ltd., Greasley Street, Bulwell, Nottingham, U.K.).
(2) Two percent KOH in ethanol.
(3) MGT reagent: 3% sulfanilamide and 0.3% N—(1 naphthyl) ethylene diamine dihydrochloride dissolved in 5% phosphoric acid, analytical reagent (AR) grade.
(4) Fixed photographic paper.

Procedure—The adhesive lifter is placed over the exhibit in the press and a pressure of *c*. 1.3 atm is applied for 5 sec (as described in Glattstein et al. (13)). The adhesive lifter is removed from the target, attached to cardboard, sprayed lightly with the KOH solution, and placed in an oven at about 100°C for an hour. The fixed photographic paper is sensitized by dipping it into the MGT reagent solution for a few seconds. The excess solution on the photographic paper is removed by wiping with a paper towel. The sensitized paper is placed on the adhesive lifter and subjected to a pressure of 1.3 atm in a press (13) at about 70°C for about 1 min. The location of stained particles is marked on the back of the transparent adhesive lifter before separating it from the sensitized paper.

Particle Sampling from the Adhesive Lifter

Smokeless powder particles are small, *c*. 0.1 mm. The minimum particle size that can be sampled is *c*. 10 μm. Skill and practice are required to manipulate the particles in order to further characterize and identify them. Sharpened needles and razor blades should be used under the microscope to handle the particles. Care should be exercised not to sample the adhesive material together with the particles from the adhesive lifter, to prevent a possible source of interference. The particles were transferred to 250 μL conical glass vials, and about 10 μL of acetone was added. The vials were vigorously agitated for several minutes.

Instrumentation

GC/MS—A Varian Star 3400CX gas chromatograph coupled with a Varian Saturn 2000 Ion Trap was used. The GC column was an Alltech-fused silica capillary column 30 m × 0.25 mm (i.d.) coated with AT-1 (0.25 μm film). The injector temperature was 250°C. The column temperature was held at 100°C for 3 min, and then heated to 250°C at a rate of 10°C/min and held for 5 min at 250°C. The transfer line was held at 170°C. The ion trap temperature was 120°C. The scan range was 25–300 Da. The scan rate was 2 scans/sec. Ionization times were set using automatic gain control. The carrier gas was helium. Injections were carried out in splitless mode. The injected samples in GC/MS were *c*. 0.5–1 μL solvent.

GC/TEA—A GC (Hewlett Packard, Model 6890), equipped with an (SGE Scientific) injector was used. The work was conducted with a 100% dimethylpolysiloxane-fused silica capillary column 30 m long, 0.25 mm i.d., and 0.25 μm film thickness. The carrier gas was helium, and the head flow was 2 mL/min (22 psi). The injector port temperature was 175°C. The oven temperature was held at 75°C for 1 min, ramped at 20°C/min to 200°C with a TEA detector as an analyzer (Thermo Electron, Model 543). The interface temperature was 300°C and the pyrolyzer temperature was 850°C. The injected samples were 1–10 μL in splitless mode.

Results and Discussion

The results of qualitative identification by GC/MS of the various components of smokeless powder are listed in Table 1.

A variety of compounds were found in the examined ammunitions. With the exceptions of 2,6-DNT and 4-NDPA by GC/MS, the qualitative compositions of the postshot after MGT treatment samples matched those of the preshot and the postshot untreated samples for each type of ammunition. Inconsistencies in detection of trace compounds such as 2,6-DNT may be related to nonuniformity in the manufacturing composition of the gunpowder. Inconsistency of 4-NDPA results may be related to changes of the gunpowder composition by burning or aging (8). Using GC/TEA, only NG and 2,4-DNT were detected, with results consistent with those obtained by GC/MS.

From the GC/MS results, it is clear that the GFL ammunition is a single-based smokeless powder as NG was not detected. The other three types of ammunition tested all contain NG and are all double-based smokeless powder. Another difference from the GC/MS results is that the three double-based smokeless powders (TZZ, Winchester Super X, and CCI Blazer) all contain EC and DNT, whereas GFL ammunition does not. The TZZ ammunition does not contain DBP and can thus be differentiated from the Winchester Super X and CCI Blazer ammunition.

The peaks without annotation in the figures were not identified as characteristic ammunition products and are mainly aliphatic products.

Figure 1 illustrates the chromatogram by GC/MS of a single-based smokeless powder (GFL). The three compounds detected are DPA, 4-NDPA, and 2-NDPA. Figure 2 illustrates the chromatogram by GC/MS of a double-based smokeless powder (Winchester Super X). A total of eight compounds characteristic of smokeless powder were detected. The compounds NG and 2,4-DNT were also detected by GC/TEA; however, many of the other compounds characteristic of smokeless powder and containing a

TABLE 1—*GC/MS results.*

Ammunition	Sample	NG	DPA	EC	MC	4-NDPA	2-NDPA	2,4-DNT	2,6-DNT	DBP
GFL	Preshot	–	+	–	–	(+)	+	–	–	–
	Postshot	–	+	–	–	+	+	–	–	–
	MGT	–	+	–	–	(+)	+	–	–	–
TZZ	Preshot	+	+	+	–	(+)	+	+	(+)	–
	Postshot	+	+	+	–	(+)	+	+	(+)	–
	MGT	+	+	+	–	+	+	+	(+)	–
Win Super X	Preshot	+	+	+	–	+	+	+	+	+
	Postshot	+	+	+	–	(+)	+	+	(+)	+
	MGT	+	+	+	–	+	+	+	+	+
CCI Blazer	Preshot	+	+	+	–	–	+	+	+	+
	Postshot	+	+	+	–	(+)	+	+	(+)	+
	MGT	+	+	+	–	+	+	+	(+)	+

NG, nitroglcerine; DPA, diphenylamine; EC, ethylcentralite; MC, methylcentralite; 2-NDPA, 2 nitrodiphenylamine; 4-NDPA, 4 nitrodiphenylamine; DNT, dinitrotoluene isomers; DBP, dibutylphthalate; MGT, Modified Griess Test; GC/MS, gas chromatography/mass spectrometry; +, present; (+), present in some of the particles only; –, not detected.

nitro group (2,6-DNT; 4-NDPA; and 2-NDPA) were not detected by GC/TEA. An obvious, inherent advantage of GC/MS is the ability to detect compounds characteristic of smokeless powder that do not contain a nitro group such as EC, DPA, and DBP.

MGT after alkaline hydrolysis leaves the powder compounds intact. After shooting, it is possible to visualize the smokeless powder residues by MGT treatment, to analyze them by GC/MS, and to deduce the ammunition components before the shooting. With the exceptions of 4-NDPA and 2,6-DNT, as already discussed, the qualitative composition of the postshot-untreated samples matches those of the postshot-treated samples. This indicates that no significant interferences occurred in the GC/MS or GC/TEA results due to the adhesive lifter sampling method.

It is recommended to mark the location of the stained particles on the back of the transparent adhesive lifter before removing the adhesive lifter from the visualized-sensitized photographic paper. The marked particles undergo microscopic examination, and only the particles with morphological characteristics typical of fired smokeless powder are analyzed.

Smokeless particles are difficult to find directly on an exhibit, such as dirty clothing of a shooting victim. Using the adhesive lifter and localization of the particles containing nitrite ions by MGT simplifies the sampling procedure for analysis and identification purposes. The adhesive lifter method was found to be suitable for clothing. It is also suitable for cadavers and objects that cannot be processed in the laboratory (14,15). The only mod-

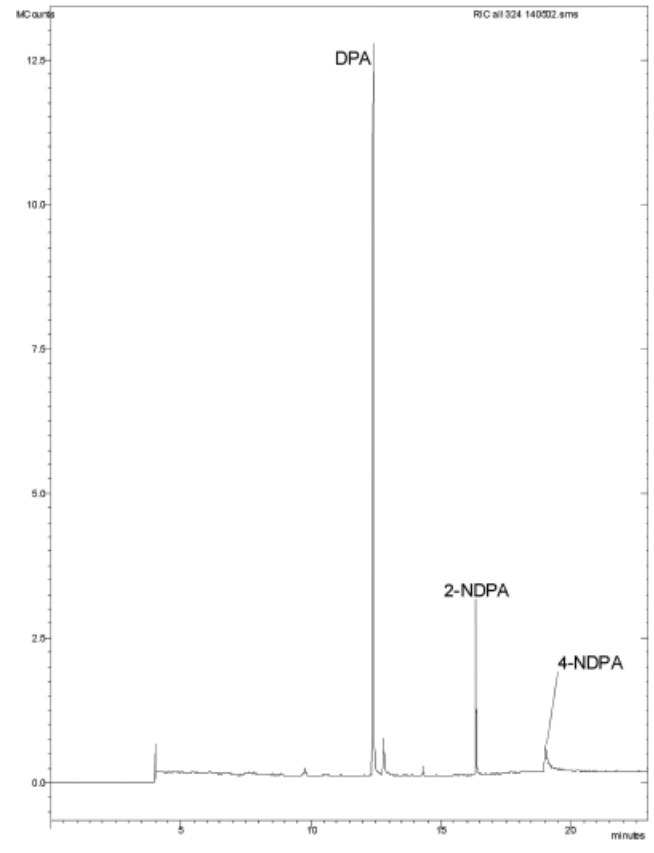

FIG. 1—*Gas chromatography/mass spectrometry of a single-base ammunition (GFL)—total ion count.*

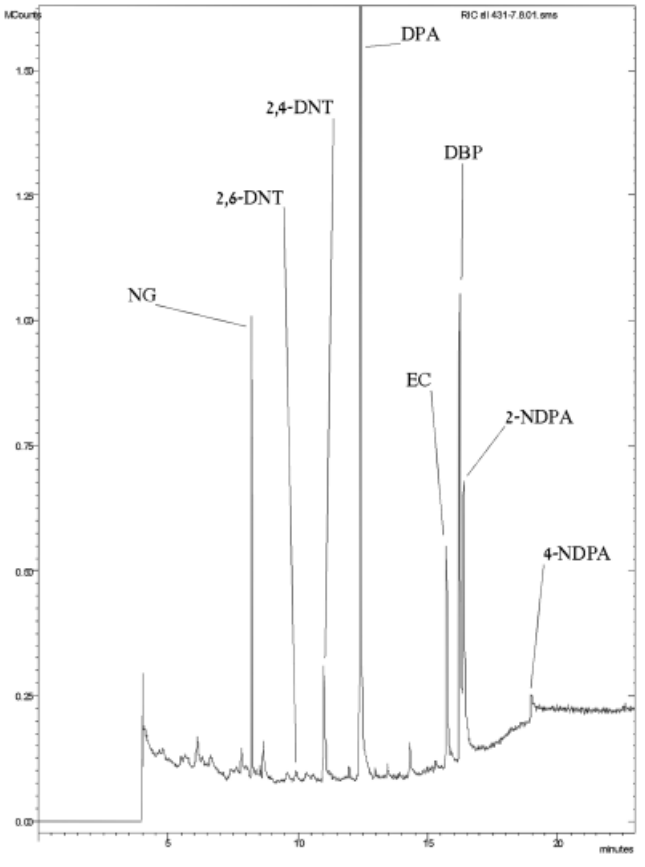

FIG. 2—*Gas chromatography/mass spectrometry of a double-base ammunition (Winchester Super X)—total ion count.*

ification necessary is that manual pressure replace the use of the press.

Conclusion

In the firing distance range of *c*. 0.75–3 m, when there are only a few particles on the target, alkaline hydrolysis followed exclusively by the MGT method is not sufficient to confirm that the particles are smokeless powder. Using the adhesive lifter to transfer the suspected smokeless powder particles followed by alkaline hydrolysis, the MGT visualization process, GC/MS, and GC/TEA analysis may confirm the chemical identification of gunpowder residues on samples as small as a single particle. GC/MS was found to be more advantageous than GC/TEA for analyzing smokeless powder residues. Depending upon the compounds identified, additional information may be obtained regarding the type of ammunition used. This new method may also confirm the origin of the nitrite group as gunpowder and negate the origin from substances such as paints or lacquers.

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