ABSTRACT

A fast LC-APCI-MS/MS screening/confirmation method was developed and validated for trace analyses of 18 analytes which are explosives and organic gun shot residues including the challenging ones with diverse ionization conditions, in soil and on hands. (+) and (−) ionization modes were used after a single-step, low-volume solvent extraction procedure developed using methanol. Tape-lifting, stub, alcohol wipes, cotton bud were compared for collecting the residues from hands of a shooter. Tape-lifting and stub gave the highest recoveries and tape-lifting was chosen. Gradient elution system using ammonium chloride:methanol was developed. Whole procedure lasted approximately 30 min, was validated in both matrices, applied to real samples as post-blast residues, smokeless powder and the hands of a shooter, after shooting. Most of the recoveries were >80% and since all the precisions were <15%, quantitation was possible for all. Limit of Detection (LOD) and Limit of Quantification (LOQ) values were: 0.2–54.1 and 0.3–190.0 ng g⁻¹ in soil, and 0.2–132.3 and 1.1–355.0 ng g⁻¹ in tape-lift.

KEYWORDS

fast LC-APCI-MS-MS analysis, explosive and OGSR in soil/tape-lift, gun-shot residues on hands, PYX, HNS, NTO, HND

INTRODUCTION

Explosives and firearms are used for wars, terrorist attacks, the mining industry and civilian purposes. Identification and characterization of trace amounts of explosives and gun-shot residues provide information to reach the perpetrator(s) of the incident. Mostly, more than one explosive is used to trigger the explosion or to increase the effect of explosion. Also the type of explosive and gunshot residues (GSR) used in the event can be determined through analysing the samples taken from the explosion zone [1, 2].

Nitroaromatic compounds including trinitrotoluene (TNT), nitrate ester compounds including cyclotetramethylene-tetranitramine (HMX) and nitramines such as hexahydro-1,3,5-trinitro- 1,3,5-triazine (RDX) are among the most commonly used explosives [3]. Nitroglycerine (NG) [4], 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) are commonly used in rocket,
missile, and gun propellants. These explosives and their derivatives are a direct risk to human health even at trace levels [5]. It is estimated that the worldwide production of explosives will reach 30 million metric tons in 2024. Since this environmental problem is an increasing concern, the detection of these compounds at trace levels is also of great importance for world public safety, as well as in the characterization of hazardous sites, forensic investigations, terrorist acts and the detection of landmines and unexploded ordnance [6]. The number of relatively new specialised explosives such as HNS, 2,6-bis(picylamino)-3,5-dinitropyridine (PYX) and 3-Nitro-1,2,4-triazol-5-one (NTO), Trimethylololethane trinitrate (TMETN), hexanitro-diphenylamine (HND), TNT, 2,6-dinitrotoluene (2,6-DNT), pentaerythritoltetranitrate (PETN), HMX, Tetryl, RDX are increasing [7, 8].

GSR analyses can support the evidence of the presence of a suspect at the crime scene, can be used in the estimate of the shooting distance, the discharge time, and the linkage of a specific weapon and/or ammunition to the incident [2]. Since different amounts of additives are used by the ammunition producers, with these analyses, it is also possible to compare the content of smokeless gunpowder, to reach its source [9]. GSRs consist of unburned and partially burnt propellant powder, particles from the ammunition primer, smoke, grease, lubricants, and metals from the cartridge. Inorganic residues originate from the primer and propellant as well as the cartridge case, the projectile jacket or its core and from the weapon barrel itself [10]. Internationally accepted method for detection and analysis of inorganic gun-shot residue (IGSR) is the scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) [11], which detects characteristic IGSR particles that include lead, antimony and barium. “Lead-free” or “non-toxic” ammunition have also been introduced to the market, regarding the concerns over health problems related to heavy metal exposure [12]. Their analysis using SEM/EDX may cause false positives; because their composition may not be specific only to firearms, it may arise from environmental/occupational effects or secondary or tertiary transfer. Thus, the analysis of organic gun-shot residues (OGSRs) has become an indisputable confirmatory tool.

OGSRs mainly come from the particles from the ammunition primer, propellant, smoke and firearm lubricants and exist in unburned and partially burned gunpowder particles [10]. Their determination supports the evidential value of a sample [12]. The main additional compounds in OGSR are several additives, stabilizers, plasticizers or flash inhibitors, coolants, moderants and surface lubricants [10, 11]. Depending on the explosive content, the gunpowders can be single base containing only nitrocellulose (NC), double base containing NC together with nitroglycerine (NG) or triple base containing NC, NG and nitroguanidine [1, 13]. The most characteristic additives of smokeless powder are diphenylamine (DPA), methyl centralite (MC) and ethylcentralite (EC), which are used as stabilizers. DPA is used in the perfume, leather, rubber and plastic industry and is not a marker for the presence of OGSR to be detected alone without derivatives (N-nitrosodiphenylamine (N-nDPA), 2-Nitrodiphenylamine (2-nDPA), 4-Nitrodiphenylamine (4-nDPA) [14].

Nowadays, most of the studies on the determination of OGSR are focused on unburned powder [12, 15]. There’s a wide variety of sampling and extraction techniques available for the collection of OGSR and explosives. However, the sampling procedures for collecting samples from the hands, hair, face and clothes of the suspect and the number of sensitive studies to detect the burnt OGSR on the samples are very few in the literature. Vacuum lifting, swab, stub, wipe and tape-lift methods were used [1, 12, 16, 17]. Solvents as methanol (MeOH) [1, 12, 18], acetone [19], acetonitrile (AcN) [20], isoamyl alcohol [21] and water [21] were used for solid-liquid extraction (SLE); for the extraction from soil [19], water [22], smokeless powders (propellant) [15, 23] and spent cartridges [1], swab or (modified) stub [12], and techniques as LC [13, 15, 24], GC [17, 25], micellar electrokinetic capillary electrophoresis (MECE) [26] time-of-flight secondary ion mass spectrometry (ToF-SIMS) [27] and desorption electrospray ionisation mass spectrometry (DESI-MS) [11] were also used.

LC/MS and LC-MS/MS methods developed for the analysis of these explosives including the specialised ones as HNS [28, 29] PYX, HND [30], NTO [20], TMETN [19] are very few. No simultaneous analysis exist in the literature, regarding the identification, quantification and validation of TMETN, HND, MC, N-nDPA, NTO, PYX, HNS, 2-nDPA, EC, 2,6-DNT, DPA, NG, 4-nDPA, TNT, RDX, PETN, Tetryl and HMX in one method, as well as soil or any collection method from hands. The ionization temperatures of some of these analytes are quiet different from each other. Heat-sensitive NG, PETN, N-nDPA [1] and TMETN [19] cannot be detected at high temperatures because they decompose, while the decomposition temperatures of PYX, TNT, HNS, DPA, NTO, HMX are high and their detectability increases with increasing temperature. Their molecular structures vary and due to their different chemical properties, different ionization techniques are needed. Also since the analytes will be in trace levels after explosion/shooting in real samples, the method should be very sensitive and specific [13, 19, 31]. These make the simultaneous analysis of these compounds challenging. Detata et al. [20], characterised over 50 organic explosives and propellants including NG, triethylene glycol dinitrinate (TEGDN), diethylene glycol dinitrate (DEGDN), TNT, RDX, HMX, PETN, Tetryl, PA, DPA, EC, PYX, HNS using LC-QToF-MS and constructed a library for detection. Solvent extracts taken from wood and plastic after controlled detonation were extracted with 10 mL AcN and the study was for qualitative detection of the explosive residues using this library. Benito et al. [12], performed the analysis of 18 explosives from the hands of shooters, including HMX, RDX, TNT, DPA, PETN, EC, diethyl phthalate (DEP), MC, dimethyl phthalate (DMP), utilizing a fast ultrasonic-assisted extraction with 1.0 mL MeOH. Swab and polytetrafluoroethylene (PTFE) tape were used to collect OGSR. The total run time including the conditioning of the column was almost 20 min. We have developed a method with a different
analyte scope in our study, where a 10 min elution time was achieved. An High Pressure Liquid Chromatography-High Resolution Mass Spectrometry (HPLC-HRMS) method was developed in 2020, using 27 analytes, synthesis by-products and additives [32]. HPLC-HRMS, X-ray Diffraction (XRD) and X-ray Fluorescence (XRF) analyses were carried out to find out the composition. Combining the results from all three techniques, 41 different additives could be identified and all samples showed a unique analytical fingerprint, allowing a differentiation. Again this differs from our study, with the samples being unexploded analytes and the method which was developed for qualitative purposes. An extraction approach was developed using LC-HRMS for trace explosives analysis in different matrices using dual-sorbent solid phase extraction (SPE) [30]. Recoveries of 44 organic explosives from model solutions were compared for seven sorbents. Validation was performed for 14 selected explosives in three matrices but not soil or any collection material from hands. The scope did not cover the analytes in the method used in this study and OGRS group. Shortly, in this study, a fast, simple, reliable and cost-effective method was developed for collection simultaneous extraction + LC-(APCI)-MS/MS analysis of 18 analytes (TMETN, HND, MC, N-nDPA, NTO, PYX, HNS, 2-nDPA, EC, 2,6-DNT, DPA, NG, 4-nDPA, TNT, RDX, PETN, Tetryl and HMX) from explosive and OGRS (TMETN, HND, MC, N-nDPA, NTO, PYX, HNS, 2-nDPA, EC, 2,6-DNT, DPA, NG, 4-nDPA, TNT, RDX, PETN, Tetryl and HMX) in two different matrices. Also, there are not much sample collection+analysis protocols developed and optimized both on explosives and OGRS. In this study, sample collection methods from hands as tape-lifting, stub, alcohol wipes, cotton bud were compared by means of extraction and collection efficiencies. Validation was performed both in soil and tape-lift. The method was further tested on real post-blast residues, real samples taken from the hands of a shower and unburned smokeless powder. Today, there’s no standard technique internationally accepted for the swabbing protocol and analysis of OGRS [33]. This study may be a pioneer to form such a procedure. The use of only one extraction+analysis method for two completely different matrices is one of the important superiorities of this study. PYX, HND, 2-nDPA qualifier ions are given here for the first time.

**EXPERIMENTAL**

**Reagents and chemicals**

HPLC Grade acetone, acetonitrile (AcN) and MeOH, HCl (37%, \(d \approx 1.18 \text{ g/cm}^3\)), NH₄Cl and picric acid (PA) were from Merck (Darmstadt, Germany, \( \geq 99.0\% \)). Explosive standards (\( \geq 98\% \)) TMETN, HND, MC, N-nDPA and NTO (100 \(\mu\text{g/mL}^{-1}\) in AcN:MeOH), PYX, HNS, 2-nDPA (100 \(\mu\text{g/mL}^{-1}\) in AcN), EC (1,000 \(\mu\text{g/mL}^{-1}\) in AcN:MeOH) were purchased from AccuStandard (USA); 2,6-DNT, DPA, NG (100 \(\mu\text{g/mL}^{-1}\) in AcN), 4-nDPA were purchased from Dr. Ehrenstorfer GmbH; TNT, RDX, PETN and tetryl were supplied by The Machinery and Chemical Industry Corporation and HMX was provided by Istanbul University Faculty of Engineering, Analytical Chemistry Department, in our previous study. Standard stock mixtures at 1,000 ngmL⁻¹ and 100 ngmL⁻¹ concentration levels containing all targeted analytes were prepared in AcN and stored at \(-18 \, ^\circ\text{C}\). Standard IS solution, mixtures and real samples were stored at 4 \( ^\circ\text{C}\).

**Apparatus**

Analyses were performed on Agilent HPLC system (Agilent Technologies, USA) coupled with 6460 QQQ-MS with API interface (Agilent Technologies, Santa Clara, CA, USA). Zorbax Eclipse Plus, 4.6 mm \( \times 100 \, \text{mm} \times 3.5 \, \mu\text{m} \) column was maintained at 15 \( ^\circ\text{C}\). Mobile phase Aaqueous solution of 0.05 mM NH₄Cl and MeOH were used in chromatographic separation at 0.8 mLmin⁻¹ flow rate: Initial composition of 90% A was decreased to 50% in 2.5 min. Then, 50% A was switched to 0% A in 5.5 min and kept for 2.0 min. After this 10 min gradient elution, column was equilibrated at 90% A for 2.5 min. Regarding the optimized MS settings; Gas temperature was 275 \( ^\circ\text{C}\), APCI heather temperature 250 \( ^\circ\text{C}\), gas flow 5 Lmin⁻¹, nebulizer pressure 55 psi, capillary voltage 3,000 and 2,500 V for positive and negative modes and APCI needle values were 4 and 20 for positive and negative modes respectively. Multiple reaction monitoring (MRM) transitions used are given in Table 1. A matrix-matched calibration technique was used to compensate for matrix effects and procedural losses.

| Analyte   | \(Q_1 \, (m/z)\) | \(Q_2 \, (m/z)\) | FV (V) | CE (V) | Polarity |
|-----------|-----------------|-----------------|--------|--------|----------|
| NTO       | 128.9           | 55.2            | 80     | 8      | Negative |
| HMX       | 330.9           | 46.0, 108.8     | 70     | 14     | Negative |
| RDX       | 256.9           | 46.2, 81.9      | 60     | 2      | Negative |
| TETRYL    | 240.9           | 181.0, 212.9b   | 90     | 2      | Negative |
| NG        | 261.9           | 62.0, 46.0b     | 50     | 2      | Negative |
| TNT       | 226.9           | 209.9, 196.9b   | 70     | 2      | Negative |
| 2,6-DNT   | 181.9           | 152.0, 46.2b    | 50     | 2      | Negative |
| HNS       | 449.9           | 240.8, 151.2b   | 100    | 8      | Negative |
| TMETN     | 289.9           | 46.1, 62.1b     | 60     | 2      | Negative |
| PETN      | 377.9           | 62.1b           | 80     | 14     | Negative |
| PYX       | 619.9           | 572.8, 496.8    | 130    | 16     | Negative |
| MC        | 241.0           | 190.8, 133.9    | 110    | 14     | Positive |
| N-nDPA    | 199.0           | 169.0, 66.0     | 60     | 6      | Positive |
| 4-nDPA    | 212.9           | 182.9, 46.2b    | 130    | 16     | Negative |
| HND       | 438.9           | 375.8, 421.8    | 100    | 12     | Negative |
| DPA       | 170.0           | 93.0, 152.9b    | 140    | 30     | Positive |
| EC        | 269.0           | 147.9, 119.9b   | 110    | 14     | Positive |
| 2-nDPA    | 213.0           | 181.9, 194.8b   | 100    | 18     | Negative |
| PA*a      | 227.8           | 197.9          | 120    | 14     | Negative |

*a IS, b Quantifier, c Qualifier.
Sample collection and preparation

**Soil extraction.** The uncontaminated soil was supplied by Istanbul University Faculty of Forestry. The pH of the soil was 7.99, the electrical conductivity was 264 uS/cm and the other tested physical and chemical properties of the test soil were as follows: The ratios of sand, dust, clay, total organic carbon content, moisture and CaCO₃ were 28.1, 18.0, 53.9, 0.8, 20.4 and 5.6% in order. The soil was grinded with mortar and pastle, dried and used as blank for method development and for validation. Blank soil was stored at room temperature. Analyte solutions were spiked to 1.0 g of soil samples in certain volumes to attain predetermined concentrations of the analytes.

In order to determine the optimum extraction solvent, standard mix solutions of the 18 analytes prepared in acetonitrile at 250.0 and 500.0 ng/mL concentrations, were spiked to 1.0 g of soil samples and MeOH, Methyl tertiary-butyl ether (MTBE), acetone and MeOH/MTBE (%75/25) mixtures were tried in extractions. Acetone was abandoned since it has dissolved the tape-lift. The effectiveness of the extraction solvents were evaluated regarding the recoveries (Fig. 1). Soil was selected in development of the extraction method, because it’s more challenging being more porous and adsorbent than other matrices. Optimum recoveries were obtained with MeOH. It was used in 4.00 mL volume, which made the method much more environmental friendly and provided an efficient extraction [11].

In the optimized sample preparation procedure; 4.00 mL of MeOH and 30.0 μL 10.0 μg/mL IS in AcN were added to 1.0 g soil. After closing the caps of the conical centrifuge tube, it was vortexed for 5 min, ultrasonicated for 15 min with caps loosened and tightened again once, and centrifuged for 5 min at 5,000 rpm. The supernatant separated was rapidly evaporated to dryness under N₂ and reconstituted using 300.0 μL MeOH. The final solution was filtered through 0.22 μm filter and injected to LC-MS/MS.

**Firearms and ammunitions.** Six different kinds of ammunition and firearms of two different calibers firearms were used for real shots. Unburned gunpowder were also analysed in 15 different ammunitions. To avoid contamination between experiments, the volunteers washed their hands properly with soap and tap water before each assay.

**OGSR sample analyses on hands (through tape-lift) and in unburned smokeless powder.** One authorized officer from Istanbul Police Headquarters performed the firearm discharges in an indoor shooting range, to evaluate the applicability of the method to real case samples. The samples were collected from back of both hands of the shooter where more firing residue exists after shooting [34]. Four sampling tools were evaluated for collection of OGSR: tape-lifting, stub, alcohol wipes, cotton bud. Stub kits of 12.7 mm diameter designed for SEM–EDX analysis of GSR were used (Adhesive Lifts GRA 200, USA). The tape layer on the stub was removed and introduced into a vial after sampling. Sample collection involving tape-lifting (50 × 60 mm) was performed through scrubbing at the shooter’s hands until it has lost all stickiness. Swabbing was performed by repeatedly scrubbing the back of hands with a cotton bud (Deltalab, Spain), moistened with MeOH. Ready to use alcohol wipes (wetened by the manufacturer with 70% v/v, isopropyl alcohol) were used in the same way.

After analysis according to the same analysis protocol developed for soil as mentioned in the subsection entitled “Soil Extraction”, cotton bud and alcohol wipes yielded the lowest recoveries. Although the stub gave close recoveries to that of tape-lift in NG and DPA, the recoveries for DPA derivatives were very low. Since the recovery for tape-lifting was higher and is routinely used by the Turkish Police, it was selected to collect samples from hands. The shooter was not allowed to touch any surface before firing. Samples were taken after three discharge. Another person was in charge of loading the gun. After firing the weapon, the hands of the shooter were sampled. After sampling, he washed his hands carefully and blank subtractions were performed, before the next shot [1, 13, 16]. To detect the probable contaminations, a blank sample was collected after the shooter has washed his hands and from a nonshooter. Unburned smokeless powder samples were collected from the ammunition boxes.

![Fig. 1. Optimization of the extraction solvent for 18 analytes in soil matrix](image-url)
The cartridge was opened and 2.0 mg of powder was taken and extracted using 4.0 mL MeOH.

Validation

Validation studies were performed with soil and tape-lifting, in terms of selectivity, specificity, linearity, Limit of Detection (LOD) and Limit of Quantification (LOQ), recovery, intra-day and inter-day precision. Specificity was assessed by observing if there was any interference from the matrix in the retention time of the analytes in each of their specific ion channel, after extracting and analysing spiked samples and their blanks. Selectivity was provided through analysing each analyte in its characteristic ion channel and the elution of each analyte in different retention times.

In validation, 1.0 g soil and 50x60 mm tape-lift (0.57 mg) samples were spiked with standard solutions. Calibration samples were prepared at 0.1, 0.5, 1.0, 5.0, 20.0, 50.0, 100.0, 250.0, 500.0, 750.0 ng g⁻¹ in soil and 0.2, 0.9, 1.8, 8.8, 35.1, 87.8, 175.4, 438.6, 877.2, 1,315.8 ng g⁻¹ on tape-lifts, through spiking 1,000.0 and 100.0 ng mL⁻¹ standard stock mix solutions to matrices in appropriate volumes, followed by spiking 100.0 µL (50.00 µg mL⁻¹) IS, where the final spiking volumes were completed to 1.0 mL using AcN. All were extracted as mentioned in 2.3.1.

Matrix effect was minimized using this matrix-matched calibration technique, where linearity and linearity ranges were determined. Minimum 3 equivalent samples were analysed at least with two injections. The standard deviations of minimum 6 individual analysis results were calculated. LOD = 3.3xs formula was used where s is the standard deviation of the repeated analyses of the samples which contained the analytes at very low concentration. The concentration corresponding to 15% relative standard deviation (RSD) from the RSD% curve drawn versus the concentration levels of calibration curves, utilizing EURACHEM method was regarded as LOQ.

Method recovery was tested comparing the analysis results where the analyte mixtures were added to the matrices before and after extraction, at low, moderate and high concentrations (250.0, 500.0, 750.0 ng g⁻¹ for soil; 438.6, 877.2, 1,315.8 ng g⁻¹ for tape-lift). Repeated analyses of each of 3 equivalent samples (number of reliable analysis results: n ≥ 4) were performed to assess the repeatabilities (RSD%). Inter-day precisions were calculated using ANOVA results (number of reliable analysis results: n ≥ 4), for two concentration levels.

RESULTS AND DISCUSSION

Development of the LC-MS/MS method

Common nitro-containing explosives and propellants undergo fragmentation via the loss of either a NO, NO₂, OH or H₂O group. Due to their different chemical properties, different ionization techniques are needed. Explosives including nitro groups commonly generate abundant negative signals. However, most of the additives used in smokeless powders such as DPA, EC and MC generate intense positive MS signals [15]. Both APCI(−) and (+) modes were used in this study, to obtain greater signal response. MRM parameters for all detected compounds are displayed in Tables 1 and 2. PYX, HND, 2-nDPA qualifier ions are given for the first time in this study.

NG, N-nDPA [1], TMETN [19] and PETN can be detected better at low gas temperatures, due to having tendency to thermal decomposition. However, the decomposition temperature of PYX, TNT, HNS, DPA, NTO, HMX is relatively high and their ionization increases with increasing temperature. Optimum temperature and voltages were implemented for vaporizing and drying gases in order to achieve efficient ionization and detection of all the analytes.

In the optimization of the LC-MS/MS method, a number of aqueous buffer solutions comprising NH₄NO₃, NH₄HCOO, NH₄CH₃COO and NH₄Cl with different concentration ranges were used. The gradient program explained in 2.2, which gave the optimum intensities for 18 analytes, was used.

Validation results

In the chromatograms of the analyte solutions and blank matrix samples, no interfering peak from the solvent or matrices and the extraction process was observed in the characteristic ion channels of each analyte, which proved the specificity. Since the retention times of analytes are different and their signals did not interfere with each other’s characteristic MRM ion channel, the method was proven to be selective. The LODs were between 0.2 and 54.1 ng g⁻¹ for soil, 0.2–132.3 ng g⁻¹ for tape-lift and LOQs were between 0.3 and 190.0 ng g⁻¹ for soil and 1.1–355.0 ng g⁻¹ for tape-lift (Table 2). The generally known relation between LOQ and LOD as follows: LOQ/LOD = 3.2. However, other ratios could be observed between these parameters, e.g. as 3.7 for NTO in soil and 1.6 in tape lift. These kind of differences may have arisen from the matrices and especially different calculation types of LOD and LOQ values which is performed through Eurachem graph for LOQ, and 3.3xs formula for LOD. Eurachem also takes into account the RSD% values at each calibration level, while the LOD calculation uses only the standard deviation of the repetitive analysis results of a very low analyte concentration. The chromatogram samples of the target analytes in soil, next to the lowest concentrations in calibration graphs are given in Fig. 2. The method showed high linearity (r² ≥ 0.99) for both matrices. Matrix effects were minimized using the matrix-matched calibration technique. The linear ranges and equations of calibration graphs in each matrix are shown in Table 3. These values indicate that the method is suitable for identification at routine casework applications. Intra and interday precisions were determined over a 3-days period with 6 replicate analyses at each concentration. Mean RSD% values were <14% for both matrices (Table 3).

The analytes have high/adequate recoveries (Table 2), except HMX and HND in soil and NG, PYX, HNS and N-nDPA in tape-lift (which were between 48 and 60%), however since the repeatability of these recoveries are quite high,
| Analyte  | Parent ion | Daughter ion | Qualifier | LOD (ng·g⁻¹) | LOQ (ng·g⁻¹) | Recovery (±SD) % |
|----------|------------|--------------|-----------|--------------|--------------|-----------------|
|          |            |              | Soil      | Tape Lift    | Soil         | Tape Lift       | Soil            | Tape Lift       |          |
| NTO      | 128.9 [M-H]⁻ | 55.2 [HCNCO]⁻ | N/A       | 1.41         | 27.7         | 26.2            | 101.5           | 42.5            | 84 (±9) 89 (±10) |
| HMX      | 330.9 [M+Cl]⁻ | 46.0 [NO₂]⁻ | 108.8 [N(NO₂)₂]⁻ | 3.93         | 18.9         | 35.3            | 38.2            | 99.5            | 49 (±10) 62 (±12) |
| RDX      | 256.9 [M+Cl]⁻ | 46.2 [NO₂]⁻ | 81.9 [C₆H₅N₂]⁺/[Cl⁻] ([NO₂]⁻) | 4.74         | 34.1         | 11.7            | 118.0           | 40.0            | 71 (±15) 81 (±9) |
| Tetryl   | 240.9 [M–NO₃⁻]⁻ | 181.0 [M–NO₂–CH₃NO₂]⁻ | 212.9 [M–CH₂N]⁻ | 5.83         | 21.6         | 45.0            | 119.0           | 79.0            | 77 (±5) 87 (±7) |
| NG       | 261.9 [M+Cl]⁻ | 62.0 [NO₃]⁻ | 46.0 [NO₂]⁻ | 6.00         | 21.7         | 31.4            | 93.5            | 43.0            | 97 (±10) 55 (±7) |
| TNT      | 226.9 [M]⁻ | 209.9 [M–OH]⁻ | 196.9 [M–NO]⁻ | 6.16         | 14.4         | 29.9            | 63.0            | 35.0            | 94 (±6) 73 (±7) |
| 2,6-DNT  | 181.9 [M]⁻ | 152.0 [M–NO]⁻ | 46.2 [NO₂]⁻ | 6.28         | 6.5          | 2.4             | 15.0            | 7.0             | 77 (±14) 96 (±10) |
| HNS      | 449.9 [M]⁻ | 240.8 [M/2–O]⁻ | 151.2 [M/2–O–NO₂–CO]⁻ | 6.67         | 17.9         | 27.3            | 100.0           | 87.7            | 84 (±11) 58 (±9) |
| TMETN    | 289.9 [M+Cl]⁻ | 46.1 [NO₂]⁻ | 62.1 [NO₃]⁻ | 6.69         | 6.5          | 19.9            | 11.3            | 56.0            | 81 (±8) 69 (±12) |
| PETN     | 377.9 [M+NO₃]⁻ | 62.1 [NO₃]⁻ | N/A       | 6.71         | 22.3         | 132.2           | 190.0           | 355.0           | 92 (±10) 68 (±9) |
| PYX      | 619.9 [M–H]⁻ | 572.8 [M–ONO–H]⁻ | 496.8 [M–H–ONO–C₆H₅]⁻ | 7.19         | 14.2         | 3.0             | 41.0            | 11.5            | 87 (±13) 48 (±5) |
| MC       | 241.0 [M+H]⁺ | 105.8 [C₆H₅NCH₃]⁺ | 133.9 [(M+1)–C₆H₅NCH₃]⁺ | 7.22         | 0.7          | 7.4             | 5.3             | 20.4            | 91 (±6) 63 (±11) |
| N-nDPA   | 190.0 [M+H]⁺ | 169.0 [M–NO]⁻ [25] | 66.0       | 7.34         | 17.7         | 5.3             | 53.0            | 41.5            | 93 (±10) 50 (±11) |
| 4-nDPA   | 212.9 [M–H]⁻ | 182.9 [M–NO]⁻ | 46.2 [NO₂]⁻ | 7.42         | 14.3         | 20.9            | 37.0            | 59.5            | 98 (±4) 92 (±12) |
| HND      | 438.9 [M]⁻ | 375.8 [M–OH–NO₂]⁻ | 421.8 [M–OH]⁻ | 7.59         | 54.1         | 30.3            | 75.0            | 59.0            | 59 (±9) 77 (±14) |
| DPA      | 170.0 [M+H]⁺ | 93.0 [M–C₆H₅]⁻ | 152.9 [M+H–NH]⁺ | 7.77         | 0.2          | 4.7             | 0.3             | 6.5             | 97 (±14) 80 (±13) |
| EC       | 269.0 [M+H]⁺ | 147.9 [M–C₆H₅N⁺]⁺ | 119.9 [M–C₆H₅N⁺]⁺ | 8.08         | 5.1          | 0.2             | 26.5            | 1.1             | 97 (±15) 81 (±12) |
| 2-nDPA   | 213.0 [M–H]⁻ | 181.9 [M–H–O₂]⁻ | 194.8 [M–OH]⁻ | 8.13         | 39.0         | 32.8            | 115.0           | 98.3            | 90 (±13) 67 (±8) b |
| PA       | 227.8 [M–H]⁻ | 197.9 [M–H–NO₂]⁻ | N/A       | 5.21         | –            | –               | –               | –               | –          |

\( n \geq 6. \\
\text{(for soil: 250.0, 500.0, 750.0 ng·g}^{-1}, \text{for tape lift: 438.6, 877.2, 1,315.8 ng·g}^{-1}).\)

b Correction factors should be used while reporting routine results.
quantitative results for the analytes with recoveries <60%, can also be reported using correction factors. Recovery correction in case of low recoveries deviating from the unity, is recommended by IUPAC to be used in the estimation of the real sample concentrations [35]. According to the SANCO/3029/99 rev.4 11/07/00 [36]; recoveries <70% may be acceptable for difficult analytes, providing that precisions are acceptable. Also UNODC Guideline [37], mention that the recovery of the analyte need not to be 100%, but the recovery range (of the analyte and internal standard) should be consistent, precise and reproducible (<20%). As indicated in part IIF, the absolute recovery (%) is not critical as long as it is reproducible and provides adequate lower limit of quantification (LLOQ).

Real post-blast and gun-shot samples

Post-blast soil samples from some of the terrorist incidents occurred in Istanbul between 2014 and 2016 after the removal of security measures, and soil samples from real shooting cases were collected at the region behind the target in open shooting area. Analysis results of residues after explosion, displayed the suitability of the method for real samples (Table 4).

Fig. 2. Chromatograms of the 18 analytes in soil next to the LOQ levels
Table 3. Linear ranges, equations of the calibration graphs and $r^2$ values, repeatability and inter-day precisions

| Analyte  | Soil     | Tape lift   | Soil     | Tape lift   | Soil     | Tape lift   | Soil     | Tape lift   | Soil     | Tape lift   |
|----------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|----------|-------------|
|          | Linear range (ngg$^{-1}$)$^a$ | Equations of the calibration graphs$^b$ | Repeatability RSD% | Intermediate precision RSD% |
|          | 500.0 ngg$^{-1}$ | 750.0 ngg$^{-1}$ | 877.2 ngg$^{-1}$ | 1,315.8 ngg$^{-1}$ | 500.0 ngg$^{-1}$ | 750.0 ngg$^{-1}$ | 877.2 ngg$^{-1}$ | 1,315.8 ngg$^{-1}$ |
| NTO      | 250.0–750.0 | 87.8–1,315.8 | $y = 0.0031x - 0.2444$ | $y = 0.0011x - 0.1429$ | 7.4 | 5.2 | 10.7 | 5.2 | 7.7 | 5.6 | 10.8 | 5.6 |
| HMX      | 50.0–750.0  | 173.4–1,315.8 | $y = 0.0007x - 0.0119$ | $y = 0.0008x - 0.0175$ | 6.6 | 5.7 | 8.6 | 5.5 | 7.0 | 5.9 | 9.1 | 5.8 |
| RDX      | 250.0–750.0 | 87.8–1,315.8 | $y = 0.0062x - 0.1850$ | $y = 0.0045x - 0.0693$ | 13.0 | 7.0 | 8.4 | 6.7 | 13.9 | 7.4 | 8.6 | 7.1 |
| Tetryl   | 250.0–750.0 | 87.8–1,315.8 | $y = 0.0045x - 0.0057x - 0.1101$ | $y = 0.0040x - 0.01317$ | 4.6 | 6.1 | 9.2 | 3.6 | 5.0 | 6.6 | 9.8 | 3.7 |
| NG       | 100.0–750.0 | 87.8–1,315.8 | $y = 0.0057x - 0.0699$ | $y = 0.0057x + 0.1317$ | 9.4 | 6.1 | 3.8 | 5.0 | 10.0 | 6.5 | 4.0 | 5.2 |
| TNT      | 100.0–750.0 | 35.1–1,315.8 | $y = 0.0077x - 0.3213$ | $y = 0.0084x - 0.0875$ | 5.0 | 3.3 | 8.1 | 4.4 | 5.5 | 3.7 | 8.5 | 4.4 |
| 2,6-DNT  | 20.0–750.0  | 8.8–1,315.8  | $y = 0.0016x + 0.0207$ | $y = 0.0014x - 0.0060$ | 7.0 | 2.5 | 6.2 | 6.7 | 7.6 | 2.6 | 6.6 | 7.2 |
| HNS      | 100.0–750.0 | 87.8–1,315.8 | $y = 0.0002x - 0.0064$ | $y = 0.0005x - 0.0207$ | 12.3 | 7.3 | 9.7 | 8.5 | 12.4 | 7.8 | 10.2 | 9.1 |
| TMETN    | 5.0–750.0   | 87.8–1,315.8 | $y = 0.0012x - 0.0187$ | $y = 0.0010x - 0.0063$ | 5.2 | 6.3 | 8.7 | 4.2 | 5.4 | 6.6 | 8.9 | 4.4 |
| PETN     | 250.0–750.0 | 438.6–1,315.8 | $y = 0.0006x - 0.0670$ | $y = 0.0002x - 0.0150$ | 9.2 | 5.0 | 7.5 | 5.9 | 9.3 | 5.2 | 7.9 | 6.2 |
| PYX      | 50.0–750.0  | 35.1–1,315.8 | $y = 0.0066x - 0.1189$ | $y = 0.0086x - 0.1828$ | 5.9 | 6.2 | 8.5 | 4.3 | 6.2 | 6.2 | 9.2 | 4.6 |
| MC       | 50.0–20.0   | 35.1–1,315.8 | $y = 0.3786x - 5.2804$ | $y = 0.2924x - 7.4610$ | 7.9 | 5.4 | 12.0 | 4.3 | 8.6 | 5.8 | 12.7 | 4.5 |
| N-nDPA   | 100.0–750.0 | 87.8–1,315.8 | $y = 0.002x - 0.021$ | $y = 0.0014x - 0.0737$ | 2.8 | 3.0 | 7.4 | 4.8 | 3.0 | 3.2 | 7.4 | 5.1 |
| 4-nDPA   | 20.0–750.0  | 87.8–1,315.8 | $y = 0.0053x + 0.0168$ | $y = 0.0051x + 0.1902$ | 3.0 | 3.8 | 7.5 | 6.9 | 3.3 | 4.0 | 8.1 | 7.4 |
| HND      | 100.0750.0  | 87.8–1,315.8 | $y = 0.0084x - 0.1171$ | $y = 0.0060x + 0.0299$ | 6.4 | 4.4 | 7.3 | 4.2 | 6.6 | 4.7 | 7.9 | 4.5 |
| DPA      | 0.5–750.0   | 0.9–1,315.8  | $y = 0.1367x - 0.0531$ | $y = 0.0674x + 0.0977$ | 4.0 | 3.4 | 5.3 | 3.0 | 4.2 | 3.4 | 5.7 | 3.2 |
| EC       | 50.0–750.0  | 1.8–1,315.8  | $y = 0.4290x - 3.266$ | $y = 0.1755x + 6.6934$ | 12.2 | 3.3 | 6.0 | 4.8 | 13.1 | 3.5 | 6.5 | 5.0 |
| 2-nDPA   | 50.0–750.0  | 175.4–1,315.8 | $y = 0.0008x + 0.0012$ | $y = 0.0008x - 0.0216$ | 7.8 | 5.1 | 7.4 | 4.6 | 8.3 | 5.4 | 7.70 | 4.8 |

$^a$ $n \geq 6$, samples $\geq 3$, injections $\geq 2$.

$^b$ Confirmed with linearity tests: $P < 0.05$, $t > t_{critical\,95\%}$. Residual errors analysis showed an appropriate regression model.

$^c$ $r^2 \geq 0.99$. 
The results show that the method can provide important information for especially on complex incidents involving firearms and explosives. In addition, combined detection of various compounds increases the evidence value of the method. The method was also able to measure the relevant compounds found in smokeless powder samples and hand swabs.

Organic explosives originating from primer and gunpowder were determined in the structure of ammunition types of different calibers from different manufacturers. Results of the analyses of unburned gunpowder and tapelifts after shooting are given in Tables 5 and 6.

No OGSR was observed during the analyses of the most of the blank samples, except some blanks from the shooter containing OGSR even after hand washing. Hand washing has previously been studied [38] and indicated a complete removal of OGSR traces. The difference in results might arise from using different soap and sanitisers. Blank subtractions were performed on every specimen of the shooter to account for possible contaminations.

Different methods have been used in the analyses of explosives and/or OGSR in literature. Our method has a superiority of using LC-MS/MS, analysing a wide array of analytes including both explosive and OGSR groups with a one-step extraction with the lowest amount of solvent which provides high recoveries in the literature. LC-MS/MS methods on multi-analyte explosive and OGSR determination especially the ones including PYX, TMETN, HND, NTO and HNS are very few in the literature. The recoveries in our study are high, and our elution time is 10 min. None of the scope of the literature studies cover the analytes in our method and OGSR group.

### Table 5. Explosives in unburned gunpowder

| Ammunitions | NG | DPA | 2-nDPA | 4-nDPA | N-nDPA | EC | MC |
|-------------|----|-----|--------|--------|--------|----|----|
| MKE 9 mm    | +  | +   | +      | +      |        | (−)| (−)|
| GFL 9 mm    | +  | +   | (−)    | (−)    | (−)    | +  | (−)|
| STR 9 mm    | +  | +   | +      | +      | +      | (−)| (−)|
| YVX 9 mm    | +  | +   | +      | +      | (−)    | (−)| (−)|
| S&B 9 mm    | +  | +   | +      | +      | +      | (−)| (−)|
| GECO 9 mm   | (−)| +   | +      | +      | +      | (−)| (−)|
| GECO 38 spec.| + | +   | +      | +      | +      | (−)| (−)|
| S&B 38 spec.| (−)| +   | +      | +      | +      | (−)| (−)|
| S&B 357     | +  | +   | +      | +      | +      | (−)| (−)|
| CCI 45cal.  | +  | +   | +      | +      | +      | +  | +  |
| Federal 45 cal. | + | + | (−) | + | + | + | + |
| MKE 45 cal.  | +  | +   | +      | +      | +      | (−)| (−)|
| 7.62 mm     | (−)| +   | +      | +      | +      | (−)| (−)|
| GFL 45 cal.  | +  | +   | +      | +      | +      | (−)| (−)|
| MKE 38 cal.  | +  | +   | +      | +      | +      | (−)| (−)|

(−): Not detected.

In application of the method to real shooting scenario, common organic components of smokeless powder and different additives coherent with NG, EC, MC, DPA and the derivatives of DPA were determined in the ammunitions. Since the initial amount of gun-free gunpowder in each fired projectile is often unknown, only identification with qualitative results were performed (Table 5). The method was able to detecting DPA along with the decomposition products and centralites (they are specific for gunpowder and an indicator of OGSR because their usage is restricted to ammunition) as a proof of a shooting with a firearm or that the person was near firearms.

### Table 6. Detected powder contents in the GSRs of selected firearms after shooting, using tapelift

| Ammunitions | Firearms | NG (ngg\(^{-1}\)) | DPA (ngg\(^{-1}\)) | 2-nDPA (ngg\(^{-1}\)) | 4-nDPA (ngg\(^{-1}\)) | N-nDPA (ngg\(^{-1}\)) | EC (ngg\(^{-1}\)) |
|-------------|----------|-------------------|-------------------|-----------------------|---------------------|----------------------|------------------|
| GFL 45 cal  | Smith    | 54.1              | (−)               | 54.1                  | 868.4               | >1,315.8             | 330.8            |
| CCI 45 cal  | Wesson   | 47.4              | (−)               | 47.4                  | 208.1               | >1,315.8             | 147.1            |
| GECO 45 cal (SW-1911) | 179.3 | (−)               | 179.3             | >1,315.8              | >1,315.8            | >1,315.8            |
| GFL 9 mm    | MKE      | (−)               | 2.3               | (−)                   | 26.1                | 260.4                | (−)              |
| MKE 9 mm    | Yavuz-16 | (−)               | (−)               | 432.5                 | >1,315.8            | (−)                 |
| S&B 9 mm    | (−)      | (−)               | (−)               | 251.6                 | >1,315.8            | (−)                 |

(−): values are well below the LOD value.
CONCLUSIONS

Regarding the studies in the literature, this is the first method/approach, identifying and quantifying the mentioned 18 analytes including both explosives and OGSRs simultaneously using one method in two matrices (soil and tape-lift sampled from hands), faster and easier than most of the methods in literature. The allorver analysis procedure takes only 30 min, which is quite attractive for routine analysis. It could also detect the target analytes in the primer and gunpowder. It’s suggested that this approach comprising sample collection + treatment + instrumental analysis, could be beneficial and be improved in the environmental contamination and forensic routine screening tests introducing more analytes.

Today, there is no standard technique internationally accepted for the analysis of OGSR. In addition, most of the analyses for the detection of OGSR in literature were made on unburned gunpowder, and the number of methods on samples taken after firing is very few. There is also no published method for the simultaneous determination of all explosive substances analysed this study. The qualifiers of PYX, HND, 2-nDPA are given for the first time in this study.

It may be possible to find the origin and the manufacturer of the ammunition in the near future, through the presentation of the primer and powder contents of different manufacturers in the library for comparison with the routine analysis results of our method in forensic cases and military studies. This study presents a validated a simple method for the simultaneous determination of all explosive substances and OGSRs, for finding the type and source of the bomb/ammunition used and to match with the suspects, in the forensic/terroristic incidents and even the monitoring of their environmental fate.

ACKNOWLEDGEMENTS

Thanks to Istanbul University Scientific Research Foundation [grant numbers: GP-10-11052006 and 23703], Ministry of Defence and the Machinery and Chemical Corporation, SEM Group, Prof. Dr. Reşat Apak and Assoc. Prof. Dr. Aysem Uzer Arda from Istanbul University Faculty of Engineering Dept. of Analytical Chemistry.

REFERENCES

1. Gassner, A. L.; Ribeiro, C.; Kobylinska, J.; Zeichner, A.; Weyermann, C. Organic gunshot residues: observations about sampling and transfer mechanisms. Forensic Sci. Int. 2016, 266, 369–78; https://doi.org/10.1016/j.forsciint.2016.06.029.
2. Taudte, R. V.; Roux, C.; Bishop, D.; Blanes, L.; Doble, P.; Beavis, A. Development of a UHPLC method for the detection of organic gunshot residues using artificial neural networks. Anal. Methods 2015, 7(18), 7447–54; https://doi.org/10.1039/c5ay00306g.
3. Chatterjee, S.; Deb, U.; Datta, S.; Walther, C.; Gupta, D. K. Common explosives (TNT, RDX, HMX) and their fate in the environment: emphasizing bioremediation. Chemosphere 2017, 184, 438–51; https://doi.org/10.1016/j.chemosphere.2017.06.008.
4. Pichiel, J. Distribution and fate of military explosives and propellants in soil: a review. Appl. Environ. Soil Sci. 2012, 2012; https://doi.org/10.1155/2012/617236.
5. Ippen, H. Toxicity and metabolism of cignolin. Dermatologica 1959, 119, 211–9.
6. Holmgren, E.; Ek, S.; Colmsjö, A. Extraction of explosives from soil followed by gas chromatography-mass spectrometry analysis with negative chemical ionization. J. Chromatogr. A. 2012, 1222, 109–15; https://doi.org/10.1016/j.chroma.2011.12.014.
7. Agrawal, J. P. Some new high energy materials and their formulations for specialized applications. Propellants, Explos. Pyrotech. Oct. 2005, 30(5), 316–28; https://doi.org/10.1002/prep.200500021.
8. Badgujar, D. M.; Talawar, M. B.; Asthana, S. N.; Mahulikar, P. P. Advances in science and technology of modern energetic materials: an overview. Elsevier 2008, 151, 289–305; https://doi.org/10.1016/j.jhazmat.2007.10.039.
9. MacCrehan, W.; Reardon, M. R. A qualitative comparison of smokeless powder measurements. J. Forensic Sci. 2002, 47(5), 1–5.
10. Dalby, O.; Butler, D.; Birkett, J. W. Analysis of gunshot residue and associated materials – a review. J. Forensic Sci. 2010, 55(4), 924–43; https://doi.org/10.1111/j.1556-4029.2010.01370.x.
11. Taudte, R. V.; Beavis, A.; Blanes, L.; Cole, N.; Doble, P.; Roux, C. Detection of gunshot residues using mass spectrometry. Biomed. Res. Int. 2014, 2014; https://doi.org/10.1155/2014/965403.
12. Benito, S.; Abrego, Z.; Sánchez, A.; Unceta, N.; Goicoeia, M. A.; Barrio, R. J. Characterization of organic gunshot residues in lead-free ammunition using a new sample collection device for liquid chromatography-quadrupole time-of-flight mass spectrometry. Forensic Sci. Int. 2015, 246, 79–85. https://doi.org/10.1016/j.forsciint.2014.11.002.
13. Laza, D.; Nys, B.; De Kinder, J.; Kirsch-De Mesmaeker, A.; Moucheron, C. Development of a quantitative LC-MS/MS method for the analysis of common propellant powder stabilizers in gunshot residue. J. Forensic Sci. 2007, 52(4), 842–50. https://doi.org/10.1111/j.1556-4029.2007.00490.x.
14. Maitre, M.; Kirkbride, K. P.; Horder, M.; Roux, C.; Beavis, A. Current perspectives in the interpretation of gunshot residues in forensic science: a review. Forensic Sci. Int. 2017, 270, 1–11; https://doi.org/10.1016/j.forsciint.2016.09.003.
15. Thomas, J. L.; Lincoln, D.; McCord, B. R. Separation and detection of smokeless powder additives by ultra performance liquid chromatography-quadrupole time-of-flight mass spectrometry. Forensic Sci. Int. 2013, 15; https://doi.org/10.1016/j.forsciint.2016.03.022.
16. Zeichner, A.; Eldar, B.; Glattstein, B.; Koffman, A.; Tamiri, T.; Muller, D. Vacuum collection of gunpowder residues from clothing worn by shooting suspects, and their analysis by GC/TEA, IMS, and GC/MS. J. Forensic Sci. Sep. 2003, 48(5), 2002390. https://doi.org/10.1520/jfs020390.
17. MacCrehan, W. A.; Layman, M. J.; Sedl, J. D. Hair combing to collect organic gunshot residues (OGSR). Forensic Sci. Int. 2003, 135(2), 167–73. https://doi.org/10.1016/S0379-0738(03)00207-X.
19. Şener, H.; Anilanmert, B.; Cengiz, S. A fast method for monitoring of organic explosives in soil: a gas temperature gradient approach in LC-APCI/MS/MS. Chem. Pap. 2017, 71(5). https://doi.org/10.1007/s11696-016-0042-2.

20. DeTata, D.; Collins, P.; McKinley, A. A fast liquid chromatography quadrupole time-of-flight mass spectrometry (LC-QToF-MS) method for the identification of organic explosives and propellants. Forensic Sci. Int. 2013, 233(1–3), 63–74. https://doi.org/10.1016/j.forsciint.2013.08.007.

21. Ali, L.; Brown, K.; Castellano, H.; Wetzl, S. J. A study of the presence of gunshot residue in Pittsburgh Police Stations using SEM/EDS and LC-MS/MS. J. Forensic Sci. 2016, 61(4), 928–38. https://doi.org/10.1111/1556-4029.13077.

22. Ochsenbein, U.; Zeh, M.; Berset, J.D. Comparing solid phase extraction and direct injection for the analysis of ultra-trace levels of relevant explosives in lake water and tributaries using liquid chromatography-electrospray tandem mass spectrometry. Chromosphere 2008, 72(6), 974–80. https://doi.org/10.1016/j.chroma.2008.03.004.

23. Dalby, O.; Birkett, J. W. The evaluation of solid phase micro-extraction fibre types for the analysis of organic components in unburned propellant powders. J. Chromatogr. A. 2010, 1217(46), 7183–8. https://doi.org/10.1016/j.chroma.2010.09.012.

24. Redouté Minzière, V.; Werner, D.; Schneider, D.; Manganelli, M.; Jung, B.; Weyermann, C.; Gassner, A. L. Combined collection and analysis of inorganic and organic gunshot residues. J. Forensic Sci. 2020, 65(4), 1102–13. https://doi.org/10.1111/1556-4029.14314.

25. Muller, D.; Levy, A.; Vinokurov, A.; Ravreby, M.; Shelef, R.; Wolf, E.; Eldar, B.; Glatstein, B. A novel method for the analysis of discharged smokeless powder residues. J. Forensic Sci. 2007, 52(1), 75–8. https://doi.org/10.1111/j.1556-4029.2006.00309.x.

26. Northrop, D. M. Gunshot residue analysis by micellar electrokinetic capillary electrophoresis: assessment for application to casework. Part II. J. Forensic Sci. May 2001, 46(3), 560–72. https://doi.org/10.1520/JFS15003J.

27. Mahoney, C. M.; Gillen, G.; Fahey, A. J. Characterization of gunpowder samples using time-of-flight secondary ion mass spectrometry (TOF-SIMS). Forensic Sci. Int. 2006, 158(1), 39–51. https://doi.org/10.1016/j.forsciint.2005.02.036.

28. Kinghorn, R.; Milner, C.; Zweigenbaum, J. Analysis of trace residues of explosive materials by time-of-flight LC/MS. Agil. Technol. Appl. Note 2006, 1–18.

29. Fu, X.; Zhang, Y.; Shi, S.; Gao, F.; Wen, D.; Li, W.; Liu, H.; et al. Fragmentation study of hexanitrostilbene by ion trap multiple mass spectrometry and analysis by liquid chromatography/mass spectrometry. Rapid Commun. Mass Spectrom. 2006, 20(19), 2906–14. https://doi.org/10.1002/rcm.2683.

30. Irlam, R. C.; Parkin, M. C.; Brabazon, D. P.; Beardah, M. S.; O’Donnell, M.; Barron, L. P. Improved determination of femtogram-level organic explosives in multiple matrices using dual-soret solid phase extraction and liquid chromatography-high resolution accurate mass spectrometry. Talanta 2019, 203(May), 65–76. https://doi.org/10.1016/j.talanta.2019.05.047.

31. Zhao, M.; Zhang, S.; Yang, C.; Xu, Y.; Wen, Y.; Sun, L.; Zhang, X.; et al. Desorption electrospray tandem MS (DESI-MSMS) analysis of methyl centralite and ethyl centralite as gunshot residues on skin and other surfaces. J. Forensic Sci. 2008, 53(4), 807–11. https://doi.org/10.1111/j.1556-4029.2008.00752.x.

32. Schachel, T. D.; Stork, A.; Schulte-Ladbeck, R.; Viehhaber, T.; Karst, U. Identification and differentiation of commercial and military explosives via high performance liquid chromatography – high resolution mass spectrometry (HPLC-HRMS), X-ray diffractometry (XRD) and X-ray fluorescence spectroscopy (XRF): towards a forensic s. Forensic Sci. Int. 2020, 308, 110180. https://doi.org/10.1016/j.forsciint.2020.110180.

33. Song-im, N.; Benson, S.; Lennard, C. Evaluation of different sampling media for their potential use as a combined swab for the collection of both organic and inorganic explosive residues. Forensic Sci. Int. 2012, 222(1–3), 102–10. https://doi.org/10.1016/j.forsciint.2012.05.006.

34. Hofstetter, C.; Maitre, M.; Beavis, A.; Roux, C. P.; Weyermann, C.; Gassner, A. L. A study of transfer and prevalence of organic gunshot residues. Forensic Sci. Int. 2017, 277, 241–51. https://doi.org/10.1016/j.forsciint.2017.06.013.

35. Thompson, M.; Ellison, S. L. R.; Fajgelj, A.; Willetts, P.; Wood, R. Harmonized guidelines for the use of recovery information in analytical measurement. Pure Appl. Chem. 1999, 71(2), 337–48.

36. European Commission, SANCO/3029/99 rev. 4 (11/07/2000) Residues guidance for generating and reporting methods of analysis in support of pre-registration data requirements for Annex II (part A, Section 4) and Annex III (part A, Section 5) of Directive 91/414. Eur. Comm. 2000, 26, [Online]. Available: https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_ppp_app-proc_guide_res_pre-reg-cont-monitor.pdf.

37. U. N. O. on Drugs, C. Laboratory, and S. Section Guidance for the Validation of Analytical Methodology and Calibration of Equipment Used for Testing of Illicit Drugs in Seized Materials and Biological Specimens: A Commitment to Quality and Continuous Improvement; United Nations Publications, 2009.

38. Arndt, J.; Bell, S.; Crookshanks, L.; Lovejoy, M.; Oleska, C.; Tulley, T.; Wolfe, D.; et al. Preliminary evaluation of the persistence of organic gunshot residue. Forensic Sci. Int. 2012, 222(1–3), 137–45. https://doi.org/10.1016/j.forsciint.2012.05.011.