

Screening of Gunshot Residues using Desorption Electrospray Ionisation Mass Spectrometry (DESI-MS)

KEYWORDS: forensic science, evidence, gunshot residues (GSR), methyl centralite (MC), ethyl centralite (EC), diphenylamine (DPA), desorption electrospray ionisation mass spectrometry (DESI-MS), scanning electron microscopy energy-dispersive X-ray detector (SEM-EDX), experimental design

Abstract

Several studies have indicated that there are potential environmental sources of particles resembling inorganic primer found in gunshot residues (GSR); as a consequence examiners are reluctant to unambiguously assign the origin of inorganic particles. If organic gunshot residues (OGSR) were found in combination with inorganic particles, the possibility of environmental sources could be potentially eliminated, thereby significantly enhancing the strength of the evidence.

Methods have been previously described whereby GSR specimens can be analysed for the presence of OGSR or inorganic GRS (IGSR). However, no methods have been reported that allow the analysis of both OGSR and IGSR on the same specimen.

Described in this article is a direct method using desorption electrospray ionisation mass spectrometry (DESI-MS) for the detection of methyl centralite (MC), ethyl centralite (EC) and diphenylamine (DPA) on adhesive tape GSR stubs typically used for scanning electron microscopy energy-dispersive X-ray detector (SEM-EDX) analysis. The optimisation of numerous parameters was conducted using an experimental design. The results indicate that direct analysis of these organic components of GSR is possible although some limitations were also identified.

This initial investigation has also indicated that subjecting stubs to DESI analysis does not interfere with subsequent SEM-EDX analysis of primer residues; therefore the technique described herein allows a comprehensive examination of GSR that would be highly probative in the event that both OGSR and IGSR are detected in the same specimen.

1. Introduction

Following events involving the suspected use of firearms, detection and identification of gunshot residues (GSR) from firearms discharge may provide important and valuable forensic information [1]. Most of the current analytical techniques are based on the analysis of the inorganic compounds found in GSR. Scanning electron microscopy coupled with an energy dispersive x-ray detector (SEM/EDX) is the most commonly used method of analysing inorganic GSR (IGSR). Its advantage arises from its ability to direct the attention of the analyst to the presence of minute, high atomic weight particles on the surface of GSR collection stubs (usually with a high level of automation) and allow elemental and morphological analysis of these particles [1]. However, several studies have indicated that environmental sources, such as paints, cars or fireworks can yield particles that resemble IGSR [2]. As a consequence, practitioners are reluctant to unambiguously assign the origin of inorganic particles as GSR [3]. Furthermore, with the relatively recent introduction of heavy-metal-free primers, there is a need to develop more comprehensive methods for the identification of GSR [4].

When a gun has been fired, GSR can arise from the primer, powder, lubricants, and metals that are found in the bullet, bullet jacket, cartridge casing, and gun barrel. The GSR originating from the primer contains inorganic elements, mainly lead, barium, and antimony. Other elements such as copper, iron, aluminium, silicon, sulphur, potassium, and calcium are also often found in GSR particles but they are more prevalent in the environment than the combination of lead, barium and antimony [5]. Organic GSR (OGSR) mainly results from the incomplete combustion of powder. Formulations of gunpowder vary based upon intended use. However, they are all designed with four main categories of ingredients: propellants (such as nitrocellulose (NC) and nitroglycerin (NG)), plasticizers, stabilizers (such as methyl

centralite (MC), ethyl centralite (EC) and diphenylamine (DPA) and flash suppressors [3,6]. Some of these organic compounds are also used in other applications, for instance, lacquers, celluloid films, varnishes and in the printing and pharmaceutical industries. However, the usage of EC and MC is restricted to ammunition and thus its detection in a forensic investigation provides strong evidence as to an association with a firearm-related event [3,7]. This is illustrated by a study conducted by Northrop [8] involving 100 volunteers representing a variety of occupations, in which none of the target organic compounds were identified on the hands of any of the volunteers.

If EC and MC were found in combination with inorganic particles indicative of primer residues, then the possibility of environmental sources of these residues could be effectively eliminated, thereby significantly enhancing the strength of the evidence.

Many analytical methods have been reported for the analysis of OGSR, such as capillary electrophoresis (CE) [8], gas chromatography-mass spectrometry (GC/MS) [9], solid phase microextraction gas chromatography-nitrogen phosphorus detector (SPME/GC-NPD) [6], liquid chromatography-tandem mass spectrometry (LC/MS-MS) [9,10], sector field high resolution inductively coupled plasma mass spectrometry (SF-HR-ICP-MS) [11] and tandem mass spectrometry (MS-MS) [12]. However, most of these OGSR methods require tedious, time consuming sample preparation. Furthermore, the main challenge faced using these techniques is that once a stub has been analysed for OGSR, it precludes the opportunity to subsequently analyse it for IGSR since these techniques are destructive. It is usually not an option to extract the stub after SEM-EDX (as the IGSR evidence will be destroyed) nor would it be particularly effective if the stub has been subjected to high vacuum. There is thus a need for an easy, rapid and non destructive screening method for OGSR to be developed which can be used prior to SEM-EDX.

Recently, ambient ionisation techniques such as desorption electrospray ionisation coupled to mass spectrometry (DESI-MS) have attracted increasing interest for the analysis of organic compounds (including some of those present in OGSR). A fundamental advantage of DESI-MS is the minimal specimen preparation requirements, the possibility to analyse minute samples in their native state and its ability for the analysis of surface deposits [3,13-17]. Coupled with MS, DESI has the potential to supply information in real time on surfaces such as stubs, skin or clothes [3]. It is thus be an ideal candidate for GSR analysis. In the DESI process, a spray of charged micro-droplets from a pneumatically-assisted needle is directed towards the surface of interest in the ambient environment. By impacting the surface, the spray desorbs the analytes into the gas phase and subsequently ionises them. The ionised compounds are then transported through the atmospheric pressure interface to the mass spectrometer and data are collected instantly [14,15,18-20].

The aim of the initial investigation reported here was to examine whether a “comprehensive” examination of GSR stubs is possible using DESI-MS for the detection of OGSR prior to SEM-EDX examination for IGSR.

2. Experimental section

2.1 Chemicals

HPLC-grade solvents, methanol (99.8%), acetonitrile (99.98%) and 1-propanol (99.8%) were commercially available from Scharlau Chemie (Spain), RCI Labscan (Thailand) and BDH hiperSolv respectively. They were used without further purification. Ultrapure water was produced by a water purification system (Sartorius, Australia). Formic acid (99% purity) was obtained through UNIVAR (Australia). Methyl centralite (1,3-dimethyl-1,3-diphenyl-urea)

and ethyl centralite (1,3-diethyl-1,3-diphenyl-urea) were purchased from Sigma-Aldrich (Sydney, Australia). Diphenylamine and nitroglycerin (1,2,3-trinitroxypropane) were sourced from Acustandard through Novachem (Melbourne, Australia).

2.2 DESI Source and Mass Spectrometry

Experiments were carried out using a Prosolia Inc. Omni SprayTM Ion Source (Indiana, US) interfaced with an Agilent Technologies 6500 Series quadrupole time-of-flight mass spectrometer (QTOF-MS) (Palo Alto, US). The DESI instrument consisted of a solvent delivery line, a coaxial nozzle for delivering the solvent, the nitrogen (N₂) nebulizing gas, a high voltage power supply, and two x,y,z-moving stages for manual independent control of both the position of the specimen and the ion source in relation to the inlet of the MS. It was operated in positive and negative modes. The DESI solvent flow rate was controlled by a Harvard Syringe Pump (Harvard Apparatus, Massachusetts, US). The nebulizing gas was sourced from BOC (Wetherill Park, Sydney). The DESI spray solvent was delivered using a Terumo 3 mL syringe, 2.3 mm diameter (Europe N.V). Instrument control, data collection and analysis were performed using Agilent MassHunter Workstation Acquisition B.02.01 software (Agilent Technologies). The temperature of the MS inlet was maintained at 350°C. Measured at the regulator, the N₂ gas pressure was maintained at 200 psi.

The DESI parameters were optimised using an experimental design and signal intensity was used as the response variable. The best results were obtained with an incident angle (α) of 55° (relative to the surface or horizontal), a spray voltage of 4 kV, a tip-to-surface distance (d_1) of 4 mm, a tip-to-sniffer distance (d_3) of 4 mm and a sniffer-to-surface distance (d_2) as small as possible (<0.5 mm).

The solvent spray was delivered to the needle by the syringe pump at a flow rate of 4 $\mu\text{L}/\text{min}$. The optimum source and parameters settings are summarized in Table 1.

Table 1

DESI-MS settings

Parameters	Settings
Electrospray voltage	+/- 4 kV
Electrospray flow rate	4 $\mu\text{L}/\text{min}$
Nebulizing gas pressure	150 psi
Incident angle (α)	55°
Collection angle (β)	< 10°
Spray tip-surface distance (d_1)	4 mm
Sniffer-surface distance (d_2)	< 0.5 mm
Spray tip-sniffer distance (d_3)	4 mm
Fragmentor voltage	175 V
Capillary temperature	350°C

2.3 Optimisation of the geometrical parameters and solvent spray composition

Initial optimisation experiments were conducted using OGSR standards. Stock solutions of MC, EC, DPA and NG were prepared in methanol at a concentration of 1000 ppm. Analytes dissolved in methanol were deposited onto a glass slide coated by heavy Teflon coating material (HTC) supplied by Prosolia Inc. 0.7 μL of a 1000 ppm solution was deposited on a HTC plate, resulting in an estimated doping area of $\sim 7 \text{ mm}^2$ and a concentration of the analytes of $\sim 260 \text{ ng}/\text{mm}^2$. The geometrical parameters (α , d_1 and d_3 distances), solvent composition and solvent flow rate were optimized using an experimental design (see below). Data analysis and calculations of the optimum function were performed using Minitab 15 Statistical Software (Minitab Inc.). The DESI-MS spectra were collected during 1.5 minutes for optimization purposes. The ion count was obtained by integrating and averaging a total of 30 seconds, consistently beginning at 30 seconds after the start of sample analysis to avoid operator bias [16].

2.4 SEM/EDX Analysis

Inorganic GSR analysis was performed on a FEI XL30 ESEM scanning electron microscope (XL Series Philips, US). The instrument was equipped with a solid-state backscattered electron (BSE) detector and EDX analysis system (EDX Control Software). The stubs were searched manually by a single operator in the BSE imaging mode and elemental analysis was obtained by EDX analysis. The accelerating voltage was maintained at 25 kV, chamber vacuum pressure set at 0.5 torr, magnification was varied between 100 and 4000x according to the particle size and the spot size set at 5 or 5.5.

2.5 Ammunition, Shooting and Sampling

2.5.1 Collection of gunshot residues on hands

In order to evaluate the potential of the DESI-MS method to analyse OGSR on stubs, test firings and GSR recovery experiments were conducted. Test firing was carried out in an indoor shooting tank at the Australian Federal Police (AFP), Forensic and Data Centre laboratories, using 5 firearms and 13 different kinds of common ammunitions. Three shots were fired with the different ammunitions and stubs (Ted Pella, Inc., California, US) were collected immediately after firing and packaged for analysis. The stub collection method involved dabbing an adhesive coated aluminium stub over the hands of the shooter until the tackiness had gone [21]. Before any firing, the shooter was asked to thoroughly wash his hands, and a control stub was taken. The ammunitions and firearms used are presented in Table 2.

Table 2

List of the ammunition and firearms used in the study

Caliber		Manufacturer	Country	Firearm used
45 AUTO		Winchester	Australia	Glock model 21 (Austria)
45 AUTO		Fiocchi	USA	
44 Magnum	Rem	PMC	Republic of Korea	Desert Eagle (Israel)
44 Magnum	Rem	Winchester	Australia	
357 Magnum .38 Spl		Winchester PMC	Australia Republic of Korea	Smith & Wesson, model 65/1 (USA)
9 mm Luger		Federal	USA	Glock model 17 (Austria)
9 mm Luger		Fiocchi	Italy	
9 mm Luger		Winchester	Australia	
9 mm Luger		Geco	Germany	
22 LR		Remington	USA	Smith & Wesson, model 17/8 (USA)
22 LR		Stirling	Philippines	
22 LR		Eley	England	

The stubs were stored under refrigeration at 4°C prior to analysis. Since DESI-MS and SEM/EDX analysis both involve analysis of the stubs in their native states, no specimen preparation was conducted¹. Half of each stub was analysed by DESI-MS in positive mode and the other half in negative mode. Data were acquired by moving the stub in a "raster pattern" for 1.5 minutes in the positive and negative modes. The stubs were then analysed by SEM/EDX in order to assess the impact of DESI-MS upon the detection of IGSR.

2.5.2 Collection and analysis of unburnt (unfired) powder

Unfired gunpowder was collected, as previously cited [6], by pulling a cartridge from the same boxes of ammunition used for the firing tests. Organic propellant components were extracted from the gunpowder by dissolving approximately 1 mg in 500 µL of methanol,

¹ It is recognised that, in real cases, the stub may need carbon coating to avoid charge accumulation due to the collection of a significant amount of non conductive material.

followed by 5 minutes of sonication and filtration through a 0.2 μm nylon filter (Econofilters, Agilent Technologies). The solution (0.7 μL) was then deposited on a HTC plate and analysed in triplicate (in the positive and negative modes).

3. Results and discussion

The experimental results showed that residues of standard solutions of MC, EC and DPA could be detected on stubs using the positive ionisation mode. Peaks at m/z 241, 269 and 170 were detected and are the corresponding protonated ions of MC, EC and DPA respectively. For an unknown reason and contrary to the research conducted by Zhao et al [3], the ions m/z 134 and 148, corresponding to typical fragments of MC and EC formed during DESI-MS process, were not detected.

The signal intensity obtained in DESI experiments is dependent on a number of operational parameters. These parameters include geometric variables (e.g incident angle (α); collection angle (β); tip-to-surface distance (d_1), sniffer-to-surface distance (d_2) and tip-to-sniffer distance (d_3)), physical variables (e.g. spray flow rate; gas pressure) and composition of the solvent. Some of these factors may be critical on the response signal of DESI-MS [22]. To reduce the number of factors and account for possible interactions between factors, a two-level fractional design was first used. This procedure was conducted in order to detect which factors were critical and had to be further optimised in order to obtain an optimal signal response. Four factors were investigated (α , d_1 , d_3 and the solvent flow rate). The gas pressure and the β angle were not varied due to the limitations of the instrumentation. Each experiment was conducted in triplicate in order to evaluate the experimental error and ensure the precision and accuracy of the results. The screening design was operated using the randomisation method [23,24]. It was found that α was not as critical as the other

factors for GSR analysis. Furthermore, changing α gave unstable and unrepeatable results. The critical parameters (d_1 , d_3 and the solvent flow rate) were then further optimised using a response surface design, in particular a modified central composite design. D_1 was varied from 2-4 mm, d_3 was varied from 4-8 mm and the flow rate from 2-4 $\mu\text{L}/\text{min}$. These particular ranges are based on preliminary experiments conducted in a scoping study (results not shown), which indicated the minimum and maximum geometrical configurations.

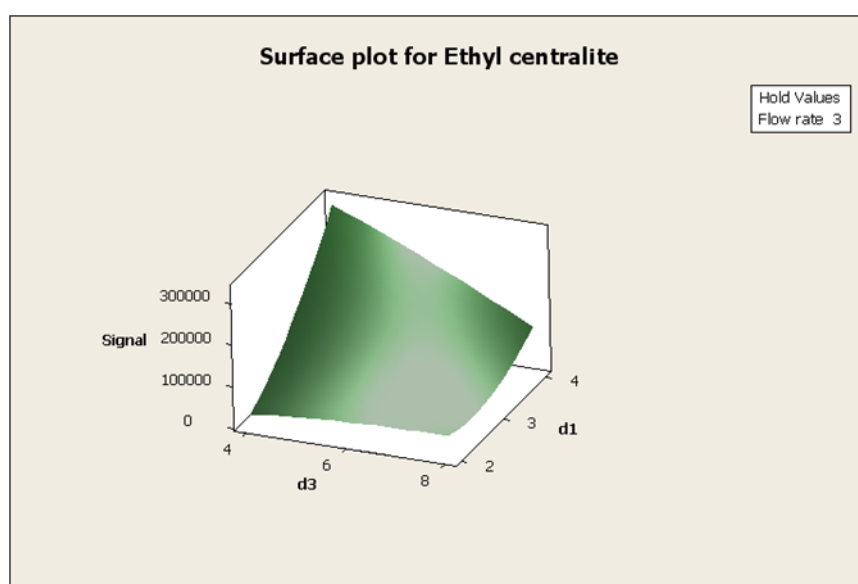


Fig. 1. Response surface plot

Figure 1 shows a response surface plot obtained for EC. It summarises the influence of d_1 and d_3 over the signal intensity of EC. The flow rate is set at mean value (i.e 3 $\mu\text{L}/\text{min}$). It provides a prediction of responses within the experimental region and allows identifying optimum conditions. The results show that a highest signal intensity and better repeatability are obtained for MC, EC and DPA using an angle α of 55° ; a tip-to-surface distance, d_1 , of 4 mm; a tip-to-sniffer distance, d_3 , of 4 mm; and a solvent flow rate of 4 $\mu\text{L}/\text{min}$. It is worth mentioning that the scoping study showed that increasing d_1 over 4 mm while decreasing d_3

under 4 mm resulted in no signal, reason why this configuration was not retained in the optimisation phase.

The solubility of the analyte in the spray solution is another essential requirement in the DESI desorption process [25]. A study from Badu-Tawiah et al [13] supports the hypothesis that the initial dissolution of the compound in the thin solvent film is crucial for stable electrospray, desorption from the surface, transfer into the gas phase and ionisation of the compound [26]. The ionisation of the analytes seems to be dependent on the polarity of the spray solvent. Polar compounds have shown to be best ionised when aqueous solvents were used, whereas for less polar compounds the best signal was obtained by using high organic content solvents [27]. Therefore, the use of an appropriate solvent is good way to improve selectivity. The purpose of the research was to find conditions that produced good sensitivity for the range of polarity classes included in this study. According to this hypothesis, a higher organic concentration in the solvent should have enhanced desorption of MC, EC and DPA and thus increased the sensitivity of the analysis.

Several solvent compositions were tested including: H₂O: MeOH (50:50) + 0.1% formic acid; H₂O: MeOH (20:80) + 0.1% formic acid; H₂O: ACN (20:80) + 0.1% formic acid; H₂O: MeOH (50:50) + 0.2% formic acid; H₂O: MeOH (40:60) + 0.1% formic acid; H₂O: MeOH (60:40) + 0.1% formic acid; H₂O: MeOH (70:30) + 0.1% formic acid; H₂O: MeOH (80:20) + 0.1% formic acid; H₂O: 1-propanol (50:50) + 0.1% formic acid; H₂O: 1-propanol (40:60) + 0.1% formic acid.

In contrast to the original hypothesis, the aqueous solvents provided superior signal intensity, with an improvement in sensitivity observed using higher water content. The precision (%RSD), however, decreased when the water content increased. However, this decrease was not significant and the %RSD was lower than 20%. A solvent composed of H₂O:

MeOH (80:20) + 0.1% formic acid provided the highest signal intensity and was thus chosen as the solvent spray.

Stubs collected after firing and unfired gunpowder specimen were analysed using the optimal analytical conditions described in Table 1. Table 3 summarises the compounds detected in the unfired powder. Nitrated-DPA are common DPA degradation products [15].

Table 3
Composition of the unfired powders

Ammunition name	Components			
	MC	EC	DPA	nitrated-DPA
Win 45 Auto		✓	✓	✓
Fiocchi 45 Auto		✓	✓	✓
PMC 44 Rem Mag			✓	✓
Win 44 Rem Mag		✓	✓	✓
Win 357 Mag		✓	✓	✓
PMC 38 Spl		✓	✓	✓
Federal 9mm Luger			✓	✓
Fiocchi 9 mm Luger			✓	
Win 9mm Luger		✓	✓	✓
Geco 9 mm Luger			✓	
Remington 22 LR		✓	✓	
Stirling 22 LR		✓	✓	
Eley 22 LR		✓	✓	

✓ Present in the gunpowder

Diphenylamine (DPA) was present in all the powders analysed, EC was present in most powders but MC was not detected. Although only a small number of powders were analysed in this research, these findings are consistent with earlier studies that found that DPA is the most common stabiliser used in smokeless powders, especially in single base powders, followed by EC whereas MC is not commonly encountered [28]. Although DPA might appear attractive as an OGSR target, its usage in products other than ammunition (such as rubber products and food [3]) precludes an unambiguous attribution of its origin. Attempted were

made to analyse stubs for the presence of NG; however, for an unknown reason, this compound could not be detected. Work towards improving the detection of additional OGSR compounds on stubs in this laboratory is continuing.

In order to test the method on real specimen, test firings were conducted and GSR collected using standard adhesive stubs. The stubs were analysed by DESI-MS using the optimised conditions reported in Table 1. Compared to experiments described above, high limits of detection were observed for EC and DPA was not detected at all (see Table 4). EC was detected in all the stubs that were known to contain EC except for the 22 LR ammunitions, which might be explained by the fact that these caliber ammunitions contain less powder and therefore yield less OGSR. It was observed that the signal intensity of EC detected on the stubs increased as its concentration in the unfired powder increased.

Table 4

Compounds found on the stubs used to collect GSR after shooting

Ammunition name	Compounds detected on stubs			
	MC	EC	DPA	nitratd-DPA
Win 45 Auto		✓		
Fiocchi 45 Auto		✓		
PMC 44 Rem Mag				
Win 44 Rem Mag		✓		
Win 357 Mag		✓		
PMC 38 Spl		✓		
Federal 9mm Luger				
Fiocchi 9 mm Luger				
Win 9mm Luger		✓		
Geco 9 mm Luger				
Remington 22 LR				
Stirling 22 LR				
Eley 22 LR				

✓ **Detected**

Compared to experiments performed on HTC plates where intense and stable signals were observed, experiments conducted on stubs generated weak and unstable signals. This could be due to the instability of the solvent layer under the high nitrogen flow, the sticky

characteristics of the stub surface, the conductivity of the stub itself or a combination of these factors [29]. The physiochemical properties of the surface are important factors in order to obtain intense signal and affect desorption and ionisation processes. This observation is consistent with previous work where HTC surfaces were found to enhance the signal intensity of small molecules in the negative and positive mode [15,30]. The use of MS-MS would likely decrease the limits of detection and increased the confidence of identification of the compound [31]. The use of MS-MS should be a good way to decrease the background noise, avoid interferences and thus obtain a lower limit of detection. Indeed, Zhao et al [3] used MS-MS and their detection limits were a lot smaller than the one obtained in this research. However, they did not analyse stubs, which is a difficult surface for the aforementioned reasons.

Weak signals could also arise as a result of test-firing and GSR collection process. Northrop et al [32] found that levels of OGSR can vary between firings carried out under the same conditions. The lack of detectable GSR may not to be an analysis issue, but rather a deposition, persistence, retention mechanism or collection issue, influenced by factors such as the type and condition of the weapons; the number of shots fired; the direction and force of air currents; and the amount of oil, moisture, or perspiration material on the deposited surface [5,32]. However, given the number of test firings conducted in this research and the uniformly low responses achieved, problems with the test-firing and collection process are unlikely.

The other aim of this research was to assess the possibility of combining DESI-MS with routine SEM/EDX analysis. Manual SEM-EDX examination of several stubs indicated the presence of particles of characteristic morphology and compositions [1]. The results must be

considered as indicative. Indeed the search was operated manually and due to time constraints, only 5-10 particles were analysed on each stub. It was found that all the stubs contained "unique" or "indicative" GSR particles [1], except for the Federal 9mm Luger ammunition. However, this can be explained by the fact that this ammunition contains a toxic, heavy metal-free primer. Most of the particles analysed had a diameter of 1-10 μm and were almost spherical. Particles with diameters of up to 30 μm were also observed.

Figures 2 and 3 show typical morphology (Fig. 2) and elemental data (Fig. 3) of a particle found on a specimen stub collected after firing a Winchester 9mm Luger cartridge. As observed, the particles contained Pb, Sb and Ba. This particular composition is usually considered as highly characteristic of GSR. However, this stub was also found to contain traces of EC (as shown in Table 4), which in the opinion of the authors substantially increases the probative value of the findings to "conclusive evidence of GSR".

This finding shows that the use of DESI-MS beforehand does not preclude the detection of IGSR by SEM-EDX. It is, however, not known if IGSR are lost during the DESI-MS process since the stubs were not analysed by SEM-EDX before carrying out DESI-MS and quantification of the number of particles was not performed.

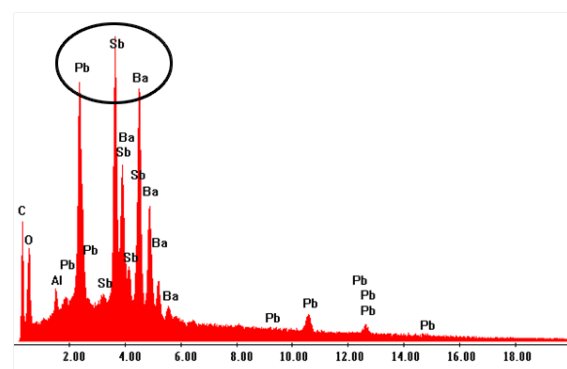
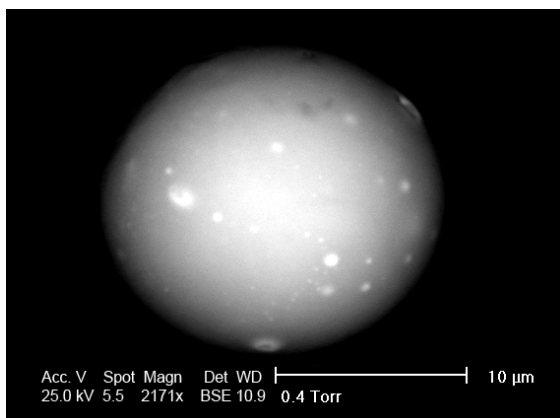


Fig. 2 and 3. BSE/SEM image (Fig. 2) and EDX spectrum (Fig. 3) of a particle found on a stub used to collect GSR after shooting a Winchester 9mm Luger cartridge

GSR detection and identification on a suspect's hands are usually performed to determine whether or not this person fired a gun (i.e. activity level). A study conducted by Wolten et al [33] showed the possibility that particles from other sources could be confused with inorganic GSR. This finding is important, especially if a sample being analysed contains only a small number of particles and these particles are not considered as unique to GSR [1]. If organic compounds could be detected in combination with inorganic elements, the evidential value in a judicial context would be higher and the likelihood of a false positive would be smaller than when using only one set of characteristics.

As mentioned by Dalby et al [5], the analysis of both organic and inorganic residues has been shown as a promising method of gaining as much information as possible from a potential GSR specimen. Furthermore, it was found that there is an approximate reciprocity between the amounts of inorganic and organic residues detected [5]. If DESI-MS on stubs could be improved with regards to the range of compounds detected and their limits of detection, it would be an ideal technique to combine with IGSR analysis in order to increase the level of information about the source.

4. Conclusion

This paper describes the first use of DESI-MS in combination with SEM-EDX analysis for the comprehensive analysis of GSR forensic specimen stubs for the presence of OGSR and IGSR. DESI-MS was demonstrated to be a rapid and easy method to detect MC, EC and DPA without any specimen preparation, with EC detected on stubs used to sample the hands of a shooter. Due to the characteristic of the stubs, the limits of detection obtained are currently

not sufficient for the technique to be used as a routine screening test for OGSR. Further research is needed, in particular in the negative mode. The use of tandem MS would also be interesting and may decrease the detection limit.

Subjecting GSR stubs to DESI-MS does not appear to adversely impact upon subsequent SEM-EDX examination of stubs for the presence of IGSR. Combining DESI-MS with SEM-EDX analysis involves very little additional time commitment, yet it offers the potential to greatly improve the probative value of analytical results. In five of the test-firings conducted, stubs were found to contain both Pb, Sb and Ba particles and traces of EC. In the absence of the organic analysis, these results would have led to an interpretation such as “particles highly characteristic of GSR were detected”. Taking the organic and inorganic results together, it can be suggested that an interpretation such as “residues conclusively identified as GSR were detected” is applicable.

Overall, the technique described in this paper offers potential and this laboratory will be pursuing its further development in order to improve the range of OGSR compounds that can be detected and the limits at which they can be detected. The final aim would be to improve the probative value still further and explore possibilities for source association.

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