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Research Article

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Analysis Gunshot Residue (GSR) – Reconstruction of Crime Scenes

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Abstract

GSR particles from the surroundings of bullet hole have been characterized as a function of primer type and particle distribution. SEM images were used to verify size and shape of the GSR particles and EDS to verify the elemental composition in a single particle. The same specimens are further subjected toTime of Flight Secondary Ion Mass Spectrometry (ToF SIMS) with a view to identify the respective surface chemistry, molecular nature and molecular mass of the GSR particles. Both inorganic and organic components of GSR in the elemental and combined form can be identified using SIMS.Secondary ion mass spectrum and the image analysis are carried out for selected particles. The mass peaks of oxides of lead, barium and antimony apart from the elemental masses are found. The combination of Pb/Ba/Sb and their oxides in a particular particle specifically establish the characteristics of a typical GSR particle. Molecular imaging and the distribution of the components in the GSR particle before and after sputtering are studied. Lead and its oxide are more concentrated in the surface of the particle compared to Ba and Sb. It is evident that SIMS can detect whether the components are either in the elemental or a compound form or a combination of both. The results of ToF SIMS clearly establish the feasibility of utilizing ToF SIMS as a tool for direct characterization of GSR from environmental polluted particles of the same nature for forensic applications.

Introduction

Several studies have been carried out in the past to characterize post-firing particles. When a gun has been fired, vapors and particulate materials can arise from the primer, lubricants and metals that are found in the bullet, bullet jacket, cartridge casing and gun barrel [1]. Gunshot residues are generated from conventional lead based primers and ammunition, composed of burnt and partially burnt particles. Cartridge primers usually consist of lead styphnate, antimony sulfide, barium nitrate, diazodinitrophenol, cellulose nitrate and tetrazene. Each manufacturer invests much time and effort in developing and providing environmentally safe or 'green' ammunition. Depending on the type and brand of ammunition, GSR particles typically contain varying amounts of lead, barium, and antimony along with other elements, such as aluminum, silicon, magnesium, calcium, potassium copper, zinc. However the high temperature and pressure that develops during the ignition of primer on firing could cause complicated chemical interactions and affects the chemical composition of the GSR [2-5]. The best tool to detect these residues remains the electron microscope combined with a energy dispersive x-ray spectrometer [6]. This technique is nondestructive and provides morphology and trace elemental composition to characterize and compare the GSR samples [7]. Particles having a spherical shape and a combination of Pb/Ba/Sb or Pb/Ba or Pb/Sb are tagged as GSR particles. However the above mentioned elements may be easily found in the environment from other sources apart from the firearm discharge. Therefore a method to study more GSR characteristics in terms of their chemical state is required to distinguish them from the elements of environmental pollution. The chemical state of the resulting GSR cannot be explained by SEM-EDX studies.

Recently a few studies are reported to explain the chemical nature of the GSR particles using XPS and ToF- SIMS (8-14). GSR on fabrics is very recently studied by Joao Carlos by inductively couples plasma spectroscopy [8]. X-ray photoelectron spectroscopy (XPS) can provide important information regarding the surface chemistry of GSR because of its nanometer-scale sampling depth [9]. The photoelectron spectrum consisting of peaks is a measure of the binding energy of the photoelectron leaving the sample. The binding energy and the shape of the peaks are characteristics of each element present in the GSR [10]. Therefore XPS compliments the SEM-EDX studies by revealing any compositional change of the primer components that may occur at high temperature and pressure during the formation of GSR particles. Schwoeble et.al studied the influence of surface chemistry on lead based GSR particles, utilized XPS to study the direct deposit discharge on a ceramic substrate after removing the projectile and the gunpowder from the cartridge [11]. They reported that elemental surface composition of GSR can vary widely between different samples produced from the same type of cartridge and between same particles on a given sample. They also found that lead in the GSR sample is present as both PbO and Pb metal and major forms of Sb and Ba found on the surfaces of GSR were Sb_2O_3 and BaO respectively.

Time-of-flight secondary ion mass spectrometry is another complementary method for the analysis of GSR particles. It is again a surface sensitive technique used to extract more information from individual GSR particles with detection limits in the part per billion ranges [12]. The sample is bombarded with a beam of primary ions and the mass of ejected secondary ions is measured via time of flight mass spectrometry. The application of ToF SIMS for the characterization of gunshot residue from 0.22 caliber rimfire ammunition is reported by John Coumbaros et.al [13]. Results have shown that GSR particles are far more complex than homogeneous lumps of metallic elements. There is evidence of layering, partitioning, and the presence of compounds such as oxides and hydroxides. Mahoney et.al published his study on the characterization and differentiation of gunpowder samples using ToF-SIMS [14].

However no much work has been done based on SIMS analysis to establish the characteristics of GSR collected directly from shooters hand or from the surroundings. It is now a common knowledge that residues from the primer should be investigated for Pb, Ba and Sb derived from lead styphnate, barium nitrate and antimony sulfide respectively. The presence of three or two metals in GSR characterizes the firing in question. But the presence of these elements in a variety of other occupational tasks questions the use of SEM/EDX alone in characterizing the GSR particles. Investigators are looking for other technique that establishes the presence of these elements in a molecular form in the GSR other than in the elemental form.

This research is an attempt to study the surface chemistry of GSR particles collected from the surroundings of bullet hole by firing cartridges consisting of lead based primers. SEM imaging is used to verify size and shape of the GSR particles and EDS to verify the elemental composition in a single particle. ToF-SIMS methods are utilized to study the surface chemistry molecular nature and the chemical composition of the GSR particle.

Methods and Materials

GSR particles were collected by firing several rounds 0.22 Remington Gold Ammunition to a cotton shirt placed at a distance of 50 cm from the shooter. The distance was selected because it represents the distance similar to real cases and also with a view to get sufficient concentration of GSR particles. The sample is then collected by touching the areas around the bullet hole with a carbon sticky tab on an aluminum stub. The tabs are carefully enclosed in a specifically identifiable box and taken to the laboratory for analysis.

Instruments

Scanning Electron Microscope/ Energy Dispersive X-ray spectrometer

The sample analysis is performed on a T-scan Scanning Electron Microscope combined with an energy dispersive x-ray spectrometer. It is a digital SEM-EDX system equipped with secondary and back scattered electron detectors, and LN2 – free XFlash Silicon Drift Detector (SDD) enabling x-ray detection of carbon and heavier elements. The EDX is equipped with Vega software which enables analyses to be conducted in the computer controlled mode once the initial instruments conditions are met.

The SEM is operated with a tungsten filament at 15 KeV acceleration voltages, 30 mm working distance and with varying magnification. The aluminum stub containing the GSR particles are manually searched in both secondary and backscattered electron imaging mode. The composition is evaluated using energy dispersive x-ray spectrometer. Spectral images are collected to have a quantitative estimation of inorganic elements in the GSR Particles.

Time of Flight Secondary Ion Mass Spectrometry

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is performed on aIONTOF Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) system. It is a surface-sensitive analytical method that uses a pulsed ion beam (Cs) to remove molecules from the very outermost surface of the sample. The particles are removed from atomic monolayers on the surface (secondary ions). These particles are then accelerated into a "flight tube" and their mass is determined by measuring the exact time at which they reach the detector (i.e. time-of-flight). Atomic weights from 1 to 10,000 amu can be detected. Analysis depth ranges from the surface, tens of angstroms down to depths of several microns. The system can detect trace elements down to concentrations of a few parts per million of a monolayer, making it only standard technique capable of dopant-level surface and depth profile characterization. It provides information about molecular, elemental and isotopic composition of the solid samples. It can also produce chemical maps and 3-D chemical reconstruction with single nanometer depth resolution and 0.1 micron lateral resolution. This instrument uses Bismuth as the liquid metal ion gun (LMIG) and Cesium/Oxygen as sputter source. The GSR sample on the adhesive carbon is placed in sample holder and then to the load lock. It is then transferred to the analyzing chamber after the load lock pressures attains 1.50 E-06.mbar. LMIG Analyzer and the Dual source column (DSC) are then powered after the analysis chamber attained a pressure of 1.9 E-09 mbar. Finally the selected area is scanned for mass spectra. Mass spectra sample the secondary ions in a preselected mass range by continuously monitoring the ion signal while scanning a range of mass-to-charge (m/z) ratios. The mass spectrum detects both atomic and molecular ions. The mass analyzer must be scanned in small steps to insure that all mass-to-charge (m/z) ratios are sampled.

Results and Discussion

Morphology

GSR particles derived from Remington Gold 0.22 caliber standard point bullets are analyzed. Shape and size of the GSR particles from the primers are carefully examined. Imaging and analysis are done without carbon or gold coating. Back scattered electron signal is used to locate the position and composition of GSR particles. These signals increase with increasing atomic number and particle appeared brighter compared to secondary electron signals. Backscattered SEM micrographs consisting of GSR particles in a large area are given in the **(figure 1a-c)**.

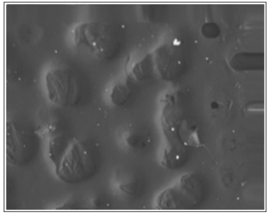

Figure 1a: Backscattered SEM photograph of GSR particles, an overall view

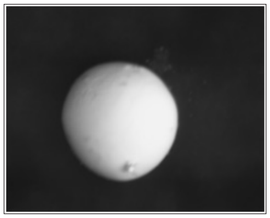

Figure 1b: Backscattered SEM photograph of a spherical GSR particle

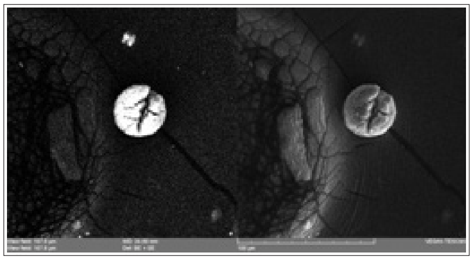

Figure 1c: Backscattered and Secondary Images of a GSR Particle

SEM micrograph of individual particles is then acquired to provide particle morphology data. Most of the particles are mainly spherical in shape and size varies from 3- 50 µm. Particle shown in figure 2has a characteristic spheroid shape and approximately 50 µm in size. Heat and pressure developed inside the gun during firing cause the primer particles to vaporize. Once they are out of the gun condenses into droplets due to surface tension and shaped spherical. However some particles of non-spherical shapes are also not unusual. These are because of the partially burnt or unburned primer emerging out of the gun along with gaseous primer particles. Most of the particles freeze due to expansion and cooling and remain small and spherical while emerging out of the gun. But a few particles grow in size due to coalescence. Spherical with dimples, oval, elliptical triangular shaped particles are also observed.

Composition

The labeled GSR particles are then subjected to the composition analysis using EDX. **(Figure 3)** is a representation of the EDX spectrum of GSR particle in figure 2. The spectrum shows that the particle consists of Copper (Cu), lead (Pb Mα), Antimony (Sb), and Barium (Ba, Lα). The presence of other elements like Al, Ca, Mg, and Si are also present apart from lead, barium and antimony.Percentage weights of each elements of interest are shown in the table1. Composition of particles is not uniform and the findings are consistent with the previous studies (2, 3) to establish the characteristics of a lead based primer.

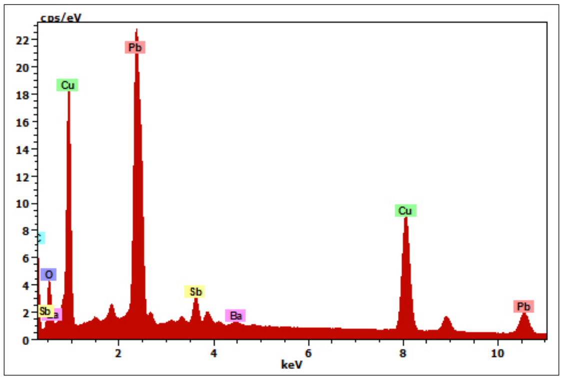

Figure 3: EDX spectrum of GSR particle

Table 1: **Quantitative analysis of the elements for the GSR particle**

El	AN	Series	unn. [wt.%]	C norm [wt.%]	C Atom. [at.%]	C Error [wt.%]
C	6	K- series	13.48	17.61	45.65	2.2
O	8	K-series	16.73	21.86	42.54	2.2
Cu	29	K-series	1.44	1.89	0.92	0.1
Sb	51	L-series	4.08	5.34	1.36	0.1
Ba	56	L-series	15.13	19.76	4.48	0.4
Pb	82	L-series	25.67	33.54	5.04	0.8

The **(figure 4)** is a representation of ToF secondary ion mass spectrum of the relative intensities of particles as a function of molecular mass. Elements detected by SIMS are Na, Mg, Si, K, Ca, Ba and Pb,. Notable molecular ions include SbO, BaO and PbO. The ion intensities reflect the isotopic abundances of the elements. Secondary ion spectrum shows that Chlorine a predominant element associated with the detection of GSR is consistent with previous studies (7). However chlorine is not detected in SEM EDX. The peak at 207 amu, 223 amu represents lead and lead oxide respectively. The other peaks in the spectrum are antimony (121.8), antimony oxide (137.8), barium oxide (154.2) copper (63.5), and calcium oxide (56.02). Amount of antimony and bariumis comparatively low which is in agreement with the EDX studies.

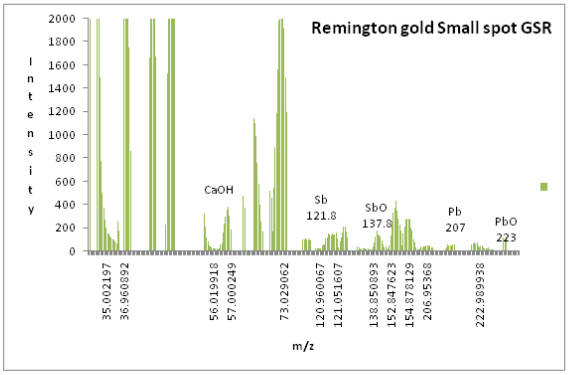

Figure 4: Time of flight Secondary Ion Mass spectrum of GSR particle

The secondary ion images **(figures 5 & 6)** illustrate the spatial distribution of elements in the selected particles. The SIMS image was taken without sputtering (figure 5) and reflects the distribution of components at the very outermost particle layer. The ion mapping reflects the visualization of the selected components in the elemental as well as in the compound form. Figure 6 represents the ion images after sputtering for 50 seconds. It seems that there is no much difference in the images morphology apart from the brightness. The ion images illustrate that the analyzed particle remains intact and the morphology remain unaltered. Findings indicate that sputtered particle is rich in antimony and barium compared to lead whereas the unsputtered is rich in lead compared to barium and antimony. It is clear that the concentrations of antimony and barium are slightly more in depth compared to the surface of GSR which is rich in lead. The nondestructive nature of TOF- SIMS makes it a highly attractive technique for forensic purposes.

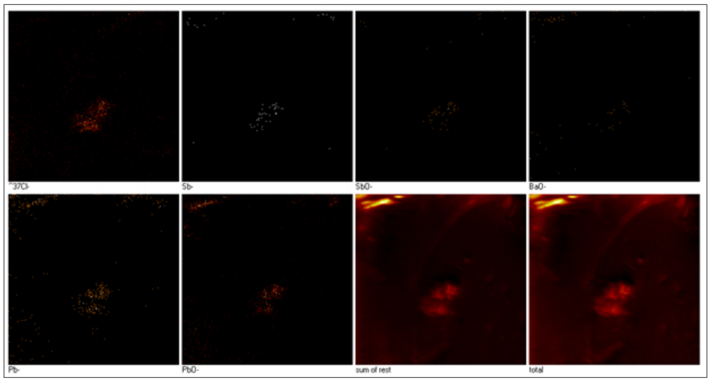

Figure 5: Time of flight Secondary Ion Mass images of GSR particle showing elemental distribution before sputtering

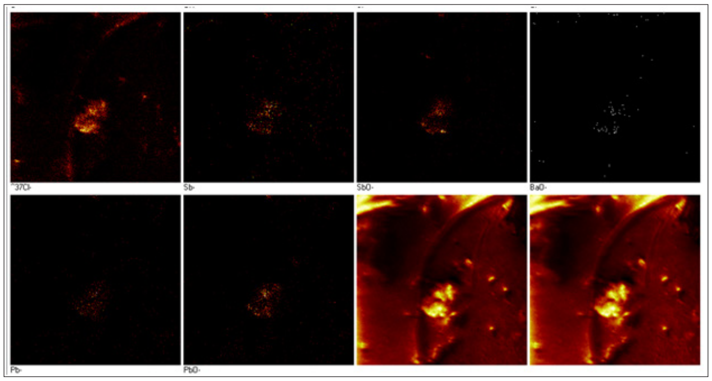

Figure 6: Time of flight Secondary Ion Mass images of sputter clean GSR particle

The secondary ion spectrum of another large particle in the same stub was given in figure 7. An irregularly shaped particle consisting of several elements Na, Si, Mg, K, Cu, Ba, Pb, Al, Ca, and Sc. characterized as compatible GSR particle. Lead and barium are in their oxide form. These particles are easily identifiable in SIMS compared to SEM.

It is well known that there are several sources that provide particles containing lead and barium like ink, brake linings, pigments and fillers in paints and plastics. It is also known that industrial power tool cartridges produce residue similar to GSR [14, 15]. SEM-TOF-SIMS provides a high degree of confidence in their classification as GSR. These particles cannot be identified as unique or typical GSR particles.

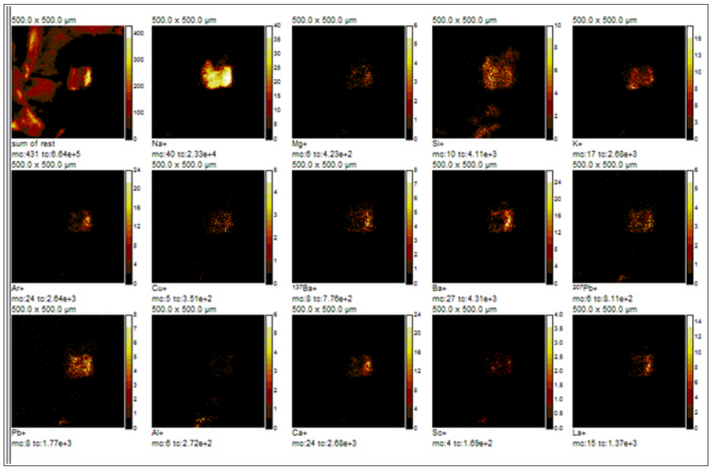

Figure 7: Time of flight Secondary Ion Mass images of a GSR particle and elemental distribution

Conclusions

SEM/EDX study provides substantial results on the shape size and the composition of GSR particles. EDX and SIMS spectra are compared to substantiate the origin of the GSR particles. Moreover the isotopic abundance of the elements in the particle is determined from the SIMS spectra which are not possible with EDX. From the SIMS results it is possible to identify the molecular nature of the elements which is important in specifying the origin of the particle. Molecular imaging technique gives more light into the fine details of the components. Sputtering can reveal the abundance of the elements in depth compared to those in the surface layer. EDX can only identify the inorganic components in the elemental form whereas TOF-SIMS could detect both inorganic and organic components. The sample collection procedure has to be modified to fit the sample in the sample holder without further modification. The advantage is that ToF-SIMS has the ability to detect traces for a wide range of elements. The main disadvantage is fixing the particle for topographic information and there is difficulty in focusing the ion gun to the exact particle due to the very small size (1-15um) of the GSR. However it is important that the ToF-SIMS can be used to complement the SEM/EDX results and to find the chemical composition. It is a means of distinguishing between real GSR particle and those derived from environmental contamination. ToF SIMS is used to compliment the EDX results [16].

Acknowledgement

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