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Case Report

A pilot study on review of GSR with a case study

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ABSTRACT

In all types of heinous crime cases like murder, homicides, assassinations, police encounter with criminal firearms are mostly involved which make important trace evidence as Gunshot residue (GSR), helps the investigating agency and forensic expert to solve and get a proper direction of investigations. Though this review article we tried to cover the how GSR form, composition and recent advancement in detection of GSR.

This pilot study will provide a hand on single article to the reader with great interest of GSR and its value in forensic investigations. The review results are in the form of impact of GSR in crime solving possibility and very interesting case study also report.

1. Introduction

1.1. Gunshot residue (GSR) where it comes from

The trace evidence interpretation, evidence dynamics and multiple transfers, of GSR, begins by defining GSR and outlining the process of its formation, before surveying the methods that have been developed to detect it. We have tried to make a comprehensive review of the experimental literature concerning the dynamics of GSR behaviour presented through the article.

A number of reviews of the GSR literature and of developments in detecting GSR particles have been carried out, yet this article differs from previous work in that it is written specifically for the purposes of this article, with a particular emphasis on transfer issues and their interpretation. This review concludes by highlighting the potential for further research into multiple transfers and contamination issues, in light of a consideration of the investigative and interpretative implications they can potentially pose in casework scenarios involving GSR.

1.1.1. Basic of gunshot residue and formation of GSR

The term Gunshot residue (GSR) is interchangeable with the less often employed terms firearm discharge residue (FDR) and cartridge discharge residue (CDR). GSR falls into the category of ‘trace physical’ or ‘trace particulate’ forensic evidence. GSR evidence is frequently utilized in the investigation of firearms offences, especially when a firearm has been discharged. It can provide a basis on which to assess different levels of proposition in the interpretation process and can be used to reconstruct a variety of facets of a firearms offence.

GSR forms when the firing pin of the gun strikes the percussion cap; initiating a chain of chemical reactions ending with the bullet being explosively propelled out the barrel of the gun. GSR is produced when a gun is fired and comprises solid ‘partially burnt and unburnt propellant particles and combustion products from the

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priming compound' along with compounds from the bullet, cartridge and firearm.[1] The composition of GSR particles results from a combination of primer and bullet derived compounds that become vaporised due to the high temperature and pressure and escape the firearm as part of an expansion plume, after which the materials cool and condense to form particles.[2]

1.2. Study on Morphology, shape and structure of GSR

The size, shape, morphology and texture of GSR particles owe much to the high temperature and pressure environment in which they are formed, and to the subsequent rapid cooling and condensing of the expansion plume. Various generic descriptions of the morphology of GSR particles have been offered and some variation exists. This variation is owing to the fact that, in reality, there is no "typical" GSR particle in terms of size and shape. However, there is generally a degree of agreement when attempting to provide definitions and descriptions that many GSR particles resemble metallic spheres, formed by the cooling and rapid solidifying of materials. Wright and Trimpe[3] report that participants of the FBI Laboratory's Gunshot Residue Symposium employed terms such as "spheroid", "noncrystalline", "condensed", "rounded", "fused", "molten" and "irregular" to describe the form of GSR particles. These terms capture the variety of GSR shapes and forms, while also reflecting the fact that near-spherical, rounded particles are common. An exterior appearance consistent with cooling and solidifying from a molten state is widely reported.[4–7] The texture of particles is readily observable using the Backscattered electron function on the SEM. Wolten et al,[8] for example, describe smooth surfaced particles, those with scaly, fuzzy exteriors, and particles that are covered in small spheres. External layering and cracking are also often observed, while it is common for GSR particles to be adhered to, or have associated with them, other materials from the firearm discharge. In terms of their size, particles may be very small and measure less than one micrometre (μm) and can also be relatively large, measuring 20μm, 30 μm, or possibly in excess of 100μm. Frequently, the majority of particles in a population of GSR will exhibit a spheroid appearance and measure in the order of a few micrometres: between <1μm and 10μm, for example.[4–7,9–12].

1.3. GSR Composition and classification

Ammunition comprises a projectile, a cartridge case, a propellant and a primer. GSR emanating from a firearm discharge will correspond, elementally, to the composition of the primer. This can be illustrated by observing the presence of lead styphnate, barium nitrate and antimony sulphide in many ammunition primers (Molina et al.[13] These compounds are responsible for the 'classic' composition of GSR - lead, antimony and barium in combination (Pb–Sb-Ba). It is the pursuit of particles with this combination that represents the most diagnostic detection of GSR. These primer contents are however, not exhaustive. Residues resulting from different primers, such as those containing mercury (Hg) will yield elemental combinations such as mercury and antimony (Hg-Sb). Meanwhile, in a recent review, Brozek-Mucha[14] refers to relatively common primers that contain mercury fulminate, potassium chlorate and antimony sulphide (after Bydal[15] and Brozek-Mucha[9]) and which produce corresponding GSR deposits.

It is acceptable, particularly within the context of this thesis, to consider the detection of a Pb-Sb-Ba ("three-component") GSR particle as the typical benchmark for a positive GSR detection. Indeed, this combination is the most commonly cited combination in the literature, and has been the focus of several decades of development with regard to its detection. Accordingly, in the latest ASTM Standard Guide for Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectrometry, E1588–10e1, this particle composition is alone in being considered to be 'characteristic' of GSR. 'Characteristic' compositions are those which are most likely to have emanated from a firearm discharge, as opposed to some other source:

The standard accounts for the fact that traces of further elements may be associated with these tri- component particles, one or more of the following: aluminium, silicon, phosphorus, sulphur (trace), chlorine, potassium, calcium, iron (trace), nickel, copper, zinc, zirconium, and tin (ASTM E1588-10e1).[16] 'Characteristic' particles are rarely recovered in great quantities without the presence of GSR particles with other compositions. These particles may contain one or two of the elements, lead, antimony and barium, as well as many other elements besides. Therefore, a host of other particle compositions are deemed consistent with GSR. Particles with these elemental compositions may originate from firearm discharge but could also be traced to other, unrelated sources. 'Consistent' compositions include:

1. Barium, calcium, silicon (with or without a trace of sulphur)
2. Antimony, barium (with or without a trace of iron or sulphur)
3. Lead, antimony
4. Barium, aluminium (with or without a trace of sulphur)
5. Lead, barium
6. Lead (only in the presence of particles with compositions mentioned thus far)
7. Antimony (only in the presence of particles with compositions)
8. Barium (with or without a trace of sulphur)

Evidently, this category of compositions is somewhat broad and clearly a firearm discharge will not represent the only source of particles with some of the compositions listed. Hence, careful interpretation is required, along with contextual information when propositions about the source of particles are being addressed. Particles cannot be considered in isolation and the presence of different compositions in the sample will also determine the evidential weight of a particular particle.

The above classifications are those most generally referred to in the literature. However, these only account for GSR generated from primers which contain compounds of lead, antimony and barium. Particles with compositions that are characteristic of such GSR can contain the following:

1. Gadolinium, titanium, zinc
2. Gallium, copper, tin
3. Other compositions are consistent with GSR originating from lead-free or non-toxic primers:
4. Titanium, zinc
5. Strontium

These compositions and classifications are not exhaustive and a particular primer may generate particles that may require additional classification. Such classifications may be generated via case-specific test firings or experimental research, but should be effective in distinguishing the GSR from environmentally or occupationally generated material of similar composition.

The elemental composition of particles within a population of GSR formed as a result of firing a particular type of ammunition will not be homogeneous. Rather, a population will include a mixture of characteristic, consistent and environmental particles. In an examination of GSR from 0.22 calibre ammunition, Coumbaros et al[17] linked the distribution of lead and barium within particles to the formation process and found that many particles exhibited a barium core that was covered by lead.

Certain exotic materials have also been found to occur within GSR and these compositional features can represent an additional discriminatory tool with which to make source level inferences. For example, Collins et al[13] observed a previously undocumented GSR particle type consisting of glass fused with the primer components. These particles were produced by firing 0.22 calibre rimfire ammunition in which the primer is sensitised with glass. The authors argue that owing to the environmental rarity of these glass-containing particles, the presence of glass in the manner described renders these particles highly characteristic of GSR and indeed, of the use of certain types of 0.22 calibre ammunition. Meanwhile, chemical taggants, such as lanthanide ions (Lucena et al[18]) which are added to some ammunition, can be identified in resultant GSR. These can assist in the determination of GSR presence and in distinguishing ammunition types, particularly with regard to identifying GSR from law-enforcement ammunition (Niewoehner et al,[19] Zeichner[20]). Owing to these compositional nuances, Dalby et al[21] advocate a case-by-case approach to identifying GSR.

1.4. The development of analytical detection methods

The use of GSR evidence in formulating and addressing different levels of proposition relating to a firearms offence relies on the analytical detection (and often quantification) of its presence. Samples may have been taken from the hands, clothing or face of a suspect, from a wound, or from surfaces at the crime scene, and these must be analysed in the laboratory. Various methods have been developed and subsequently employed in this process, each with their own strengths and drawbacks. The various GSR detection methods reported in the literature rely on the detection of certain elements, often lead, barium and antimony in some combination. Wet chemical tests (Harrison and Gilroy[22]) provided confirmation regarding the presence of lead, barium and antimony, while earlier tests confirmed the presence of their nitrates (Romolo and Margot[23]). These tests along with paraffin cast examinations, while rapid, easily executed and inexpensively conducted, were found lacking in their sensitivity and in their GSR specificity. Further techniques that have been widely employed in the detection of GSR and that have undergone significant development and refinement include instrumental methods such as neutron activation analysis (NAA) (Ruch et al,[24] Rudzitis et al,[25] Krishnan[26], Saferstein[27]) and atomic absorption spectroscopy (AAS) (Krishnan et al,[28] Koons et al.[29]) A method involving photoluminescence has also been explored (Jones and Nesbitt,[30] Nesbitt et al.[31]

Further methods that have been trialled, developed and utilised for the detection of the inorganic fraction of GSR include X-ray microfluorescence (Brazeau and Wong[32], Flynn et al 1998[33]) inductively coupled plasma mass spectrometry/atomic emission spectroscopy (ICP-MS/AES) (Koons,[34] Koons et al.[29] as well as anodic stripping voltammetry (ASV) (Liu et al[35]) (Romolo and Margot[23]). All of the methods described exhibit a number of drawbacks. Moreover, they are not sufficiently sensitive to permit the identification and quantification of the elemental contribution of individual (GSR) particles (Tillman[36]).

2. Methodology

Energy dispersive X-Ray fluorescence (EDXRF).

A schematic representation of an EDXRF spectrometer setup is shown in Figure 1. The setup of EDXRF instrumentation is quite simple, consisting of four basic components,

1. Excitation source,
2. Sample,
3. Detector, and

4. Data collection and analyzing system.

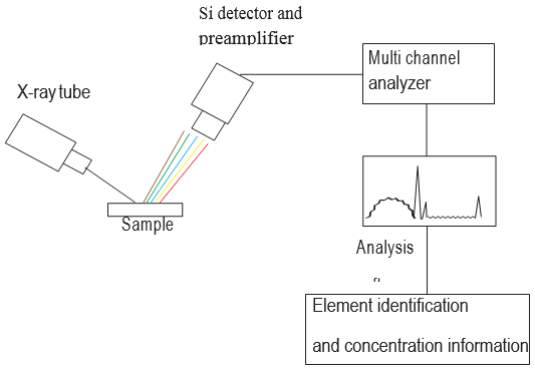

Fig. 1: The schematic of an EDXRF Spectrometer. The X-rays from the source irradiate the sample, characteristic X-rays are detected by the Si detector, the multi channel analyzer separates different elemental peaks and the analysis software gives the final list of elements and their concentrations

The EDXRF spectrometer helps plotting the relative abundances (in terms of intensities) of characteristic X-rays versus their energy. The characteristic X-rays generated strikes the detector element (in this case Silicon), creating an electron hole pair, which produces a charge pulse proportional to the energy of the X-ray. This charged pulse is converted to a voltage pulse by a charge sensitive preamplifier. A multi channel analyzer (MCA), is then used to analyze these pulses and sort them according to their voltages. This data is then sent to the computer interface, where it is displayed as the spectrum of the X-ray irradiated sample. The spectrum is further processed to identify elements and quantitatively analyzed to find the respective concentrations in a sample.

2.1. Our set – up

Incorporating a high-performance semiconductor detector, the EDX-7000/8000 spectrometers offer excellent sensitivity, resolution, and throughput for an array of applications, from general screening analysis to advanced materials research.

The calibration samples were generated from a water solution spiked at seven concentrations, including zero concentration (pure water), of Cd, Pb, As, V, Co, and Ni using standard solutions for atomic absorption spectroscopy. The verification samples were generated from cellulose powder spiked at two concentrations of the above six elements using standard solutions for atomic absorption spectroscopy. The standard solutions were added to the blank cellulose samples and mixed in an agate mortar to prevent adhesion to the walls. In order to check for homogeneity, a small amount of each spiked cellulose sample was taken and divided into three subsamples, which were measured for the quantitative amounts of target elements present. The three subsamples were then mixed together before being re-divided into three new subsamples for measurement. The mixing, division into three, and measurement were then repeated (nine measurements in total). If the quantitative values of target elements were consistent for the different subsamples, then the sample was regarded as homogeneous. All the features of the instrument are available in the Manual and reported in the chapter in (Figure 3 a-e) as from Shimadzu Manual. [15]

Measurement Technical Specification reported the Table – 1 of the set-up used in the analysis EDX – 8000 Shimdzu, USA:

Measurement principle	X-ray fluorescence spectrometry
Measurement method	Energy dispersion
Target samples	Solids, liquids, powders
Measuring range	$_{11}$Na to $_{92}$U (EDX-7000) $_{6}$C to $_{92}$U (EDX-8000/8100)
Sample size	W 300 × D 275 × approx.H 100 mm (excluding radiuses)
Maximum sample mass	5kg (200g per sample when using turret, Gross mass 2.4kg)
X-ray generator	
X-ray tube	Rh target
Voltage	4 kV to 50 kV
Current	1 μA to 1000 μA
Cooling method	Air-cooled (with fan)
Irradiated area	Automatic switching in four stages: 1, 3, 5, and 10 mm diameter Automatic switching in four stages: 0.3, 1, 3, and 10 mm diameter*1
Primary filters	Five types (six, including the open position), automatic replacement
Detector	
Type	Silicon drift detector (SDD)
Liquid nitrogen	Not required (electronic cooling)
Sample chamber	
Measurement atmosphere	Air, vacuum*1, helium (He)*2
Sample replacement	12-sample turret*1
Sample observations	Semiconductor camera
Data processor	
Memory	2 GB min. (32-bit), 4 GB min. (64-bit)
HDD	250 GB min.
Optical drive	Super multi drive
OS	Windows 10 (32-bit/64-bit)*3
Software	
Qualitative analysis	Measurement/analysis software
Quantitative analysis	Calibration curve method, correction for coexistent elements, FP method, film FP method, background FP method
Matching software	Intensity/content
Utilities	Automatic calibration functions (energy calibration, FWHM calibration)
Others	Instrument status monitoring function, analysis results tabulation function
Installation	
Temperature	10 °C to 30 °C (temperature fluctuation rate 2 °C/hour max., temperature fluctuation range: 10 °C max.)
Relative humidity	40 % to 70 % (no condensation)
Power supply	100-240 V AC ±10 %, 2 A earthed socket
Dimensions	W 460 × D 590 × H 360 mm
Weight	Approx. 45 kg

*1 Option for EDX-7000/8000/8100

Fig. 2: Specification of the set-up EDX - 8000

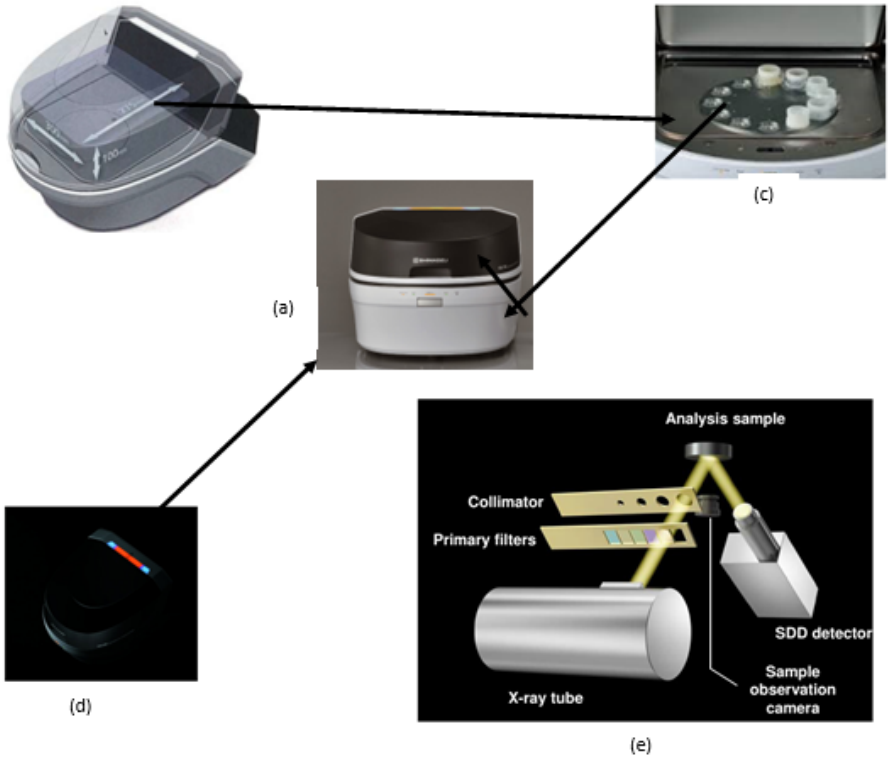

Fig. 3: (**a**) Showing the image of EDX – 800; (**b**) Showing the schematic image with sample chamber dimensions 300 mm × 275 mm × approx. 100 mm; (**c**) 12-Sample Turret ; (**d**) Easy-to-see LED indicators (Red: X-rays ON Blue: Analyzing) and (**e**) Schematic concept of X-ray fluorescence (XRF) in the EDX – 8000

Fig. 4: **a**): Room where the crime was occur; **b**): Bear foot with blood smear; **c**): Dead bodies lying the bathroom; **d**): Firearm with fired bullet cartridge and **e**): First bullet cartridge found in washbasin of the bath room

Images of the set-up with all specific feature has been shown in Figure 3.

3. Case Study

3.1. Murder and then committing suicide

In this case a male murdered a lady in the bathroom and committed suicide near the dead body of the lady. This involved scientific crime scene investigation, interpretation of patterned evidence at the scene, laboratory testing of the physical evidence GSR, systematic study of related case information, and the logical formulation of a theory gives the proper directions to the Investigating officer (IO). The case published,[37] on the basis of our findings of our team, reveals the truth and case was solved at scene of crime. Otherwise, IO was in another impression of the Scene of occurrences. As per IO, It was a murder mystery. On the bases of our fourfold observations, 1) the entry of the hotel room was closed from the inside; 2) blood droplet on the tool bag of the person having blood drop; 3) one cartridge case was found in the firearm and one in the washbasin; 4) bare foot marks of the male on the floor 5) Prelim – GSR on hand, prove that the firearms was used by the male only.

4. Conclusion

GSR evidence is one of the most common trace evidence examined in crime investigation. GSR examination is done is Forensic Science Laboratory in India with very high accuracy and modern analytical techniques. This study will provide a comparable data to the scientist to take as reference in Indian contest. The specific study on GSR for Indian ammunition using country made firearms has not been reported yet.

The GSR analysis of lead, can be used as an indicator of the presence of the residues. For the assessment of the value of a GSR is linking a suspect and a crime, it is importance to compare two hypotheses: the first can be that of the evidence if the suspect has been shooting in as specific situation, the second that of the evidence if the suspect was not involved in the shooting.

5. Source of Funding

None.

6. Conflict of Interest

None.

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