

Detection of GSR with the help of Nanoparticles : A Review

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ABSTRACT

GSR (Gunshot Residue) also known as gun powder highly found as evidence on the crime scene. Combination of unburnt and partially burnt propellant powder as well as particles from the ammunition, primer, smoke, grease, lubricants and metal from the cartridge. The detection process of GSR and the test performed are very lengthy and time taking due to which investigation gets slower and cases are pending. Use of nanoparticles for the detection of GSR can make the process quick and easy in primary survey.

Keywords: GSR, Nanoparticles, crime scene, evidence, gun powder, investigation.

I. INTRODUCTION

This article is a review of the different types of tests used in detection of GSR, which is found on crime scene on different surfaces. GSR is the primary evidence found on the crime scene and plays important role during the investigation and court trails.

The GSR is found distributed on hand. The richest source is on web of hand between thumb and index finger. The GSR is found in decreasing amount on outer surface of thumb, on the back of index finger and outer surface of hand and finger.

GSR may also include essence fractions from the cartridge containing the pellet jacket, as well as any other dirt or residue contain within the barrel that could have come dislodge. GSR doesn't travel very far because the flyspeck produces are of small size and small mass therefore causing them lack of instigation. Depending on the type of fire arm and security used, it'll generally travel no further than 3- 5 bases (0.9-1.5 meters.)

The present work describes an innovative handheld device for rapid-fire discovery of Lead (Pb₂) in Projectile remainders (GSR). Our system is veritably sensitive, picky and specific for not only qualitative but also quantitative discovery of Pb₂ in colourful

GSR samples. It's grounded on the principle of shift in Light Scattering Plasmon Resonance (LSPR) of Poly Vinyl Alcohol (PVA) Capped Silver Nanoparticles (AgNPs) from 410.5 nm to 590 nm which do due to strong ion dipole commerce between Pb²⁺ and PVA limited tableware nanoparticles leading to change in colour. Colourful parameters were optimized and characterized using several instruments. Qualitative discovery was made visually by naked eyes with a change in colour using micro-Liter of samples. Colourful GSR samples were collected from different security fired at varying range on cloth piece. The results were compared and identified with standard given styles similar as infinitesimal immersion Spectroscopy (AAS) and UV – Vis spectroscopy (1). The system showed linearity in the range from 0.01 to 10 ppm with limit of discovery (LOD) of 1.02 ppm ($R^2 = 0.98$). No snooping effect was observed in the presence of several other essence ions similar as Cu²⁺, Mg²⁺, Ca²⁺, Ba²⁺, Hg²⁺, Cr³⁺ etc (1). This low cost, rapid-fire, colorimetric system tested using handheld device for Pb²⁺ discovery in GSR underlines the onsite connection of this system and helpful in determining the range and type of security used which would further help forensic scientist.

Analysis of Gun- Shot Residue (GSR) is a veritably critical step in Forensic studies of firing and affiliated felonious cases. Still, the current ways used for GSR analysis aren't complete. Detailed information regarding the essential and crystallographic autographs of the GSR is missing. Also, the analysis requires a substantial quantum of sample which is delicate to gain and constantly might be defiled. The current study on the GSR focuses on these scarcities. Electron bitsy studies of the metallic nanoparticles (10- 100 nm in periphery) attained from GSR at different target distances from a Winchester Super-X 9 mm luger has been anatomized in detail. Impeccably globular (periphery 10 nm) and veritably liquid Pb and Sb nanoparticles (2) were observed. Theoretical studies explaining the conformation of the nanoparticles is reported. Thonon-equilibrium

thermodynamic processes leading to the conflation of the nanoparticles was observed to be veritably analogous to the artificial chemical conflation styles (e.g. CVD, Ray Ablation etc.). A simplified model will be proposed to explain the nanoparticle conflation process in the GSR. This fresh information attained from the nanoparticle conflation model will give precious forensic substantiation in working felonious cases. Forensic benefits of this information will be bandied. This ingenious conflation medium has been demonstrated in synthesizing pure crystalline form of other popular nonmaterial. (2)

Projectile remainders (GSR) from an aggregate of nine different quality protections produced in Brazil were anatomized and characterized by transmission (TEM) and surveying electron microscopy (SEM). GSR patches are composed of globular patches of several micrometres of periphery containing distinct quantities of lead, barium and antimony, along with other organic and inorganic rudiments arising from the manual, gunpowder, the gun and the pellet itself. This study was carried out to gain fresh information on the parcels of GSR nanoparticles began from different types of regular security produced in Brazil by CBC. Besides the SEM, we've used a TEM, exploring its high exaggeration capability and capability to explore internal structure and chemical composition of submicron patches. We observed that CBC security generated lower patches than generally reported for other protections and that the three element patches aren't a maturity. TEM analysis revealed that GSR are incompletely composed of sub-micron patches as well. The electron diffraction pattern from these patches verified them to be substantially composed of lead oxides liquid nanoparticles that may be rolled into larger patches. Energy dispersive X-ray spectroscopy revealed that utmost of them were composed of two rudiments, especially PbSb. Ba wasn't a common element set up in the nanoparticles.

Single Flyspeck inductively coupled tube mass spectrometry (spICP- MS) was delved as a webbing-

position fashion for the analysis and characterization of inorganic projectile residue (IGSR) nanoparticles. spICP- MS works with undigested samples whereby nanoparticles (NPs) in a suspension are collectively comminuted and ionized as they reach the tube, each performing in a palpitation of analyte ions that can be quantified. The system is rapid-fire, and signals from hundreds of NPs can be collected in 1 – 2 min per sample (3). The fashion is quantitative for NP mass and number attention when only one element (single element mode) is measured using a quadrupole MS. Likewise, a qualitative essential point can be attained for individual NPs when peak- hopping between two rudiments (binary element mode) (3). For this evidence of conception study, each shooter's hand was tried with ultrapure water or tar to gain NPs dormancies. measures of antimony, barium, and lead were performed using both analysis modes. With no sample medication and completely automated sample preface, it's possible to dissect further than 100 samples in a day. Results show that this fashion opens a new perspective for unborn exploration on GSR sample identification and characterization and can round SEM/ EDX analysis. (3)

Nitrite ions are important labels in projectile residue (GSR) analysis. A largely sensitive and picky detector that precisely identifies nitrite ions still needs to be developed. This work thus proposed a new approach for nitrite ion discovery grounded on the oxidative drawing of cetyltrimethylammonium ammonium platitude- stabilized gold nanoparticles (CTAB@AuNPs) (4) by nitrite ions to induce gold ions (Au³⁺), which can beget the corruption of hydrogen peroxide and further reply with fluorogenic substrates (o- phenylenediamine OPD) to yield effective fluorescent species (2,3- diamino phenazine; DAP). The attention of nitrite ions can be laterally determined by tracing the luminescence intensity of the generated DAP. The degrees of luminescence improvement increased linearly with adding nitrite ion attention in the attention range of 0 – 60 μM , with a minimal limit of discovery (LOD) of 0.07 μM . More

importantly, only nitrite ions can beget this luminescence improvement, while other tested anions showed no significant effect. Compared with the reference system, the proposed detector can be applied for the discovery of nitrite ions in GSR with satisfactory results. (4)

This manuscript describes an innovative hand-held device for the rapid detection of barium (Ba²⁺) in gunshot residue (GSR) based on the use of gold nanomaterials coated with sodium malonate (5). The method relies on the shift of the light-scattering plasma resonance (LSPR) peak of malonate gold nanoparticles (AuNPs) from 526 nm to 610.5 nm due to the aggregation of carboxylate ions between the metal and the nanoparticles resulting in a colour change. Qualitative detection was realized by colour change, while for quantitative analysis a hand-held device was made in-house. The results were then correlated with those of standard known methods such as UV-Vis's spectroscopy and inductively coupled plasma optical emission spectroscopy (ICP-OES). The results showed a better correlation between the manufactured device and the standard methods with R² = 0.98. It exhibits a linearity range from 0.01 mg ml⁻¹ to 5 mg ml⁻¹ with a limit of detection (LOD) of 0.2 mg ml⁻¹. (5) In addition, GSR samples were taken from a set of cloth pieces at different firing distances (i.e., 1 ft to 16.40 ft) using different ammunition to detect the presence of Ba²⁺ with the help of the developed device and the results were similar to known methods. The handheld device was found to be unaffected by other interfering substances (i.e. Pb²⁺, Sb³⁺, Ca²⁺, Cu²⁺, Hg²⁺, Mg²⁺, As³⁺, Cr³⁺, etc.). The results demonstrated here demonstrate a high selectivity, sensitivity, and rapid method for the detection of Ba²⁺ in GSR, indicating its greater potential for the future. (5)

Projectile residue (GSR) is a miscellaneous pall of vapours and generates from the explosive material present in the cartridge. Whenever an arm is used in the crime, Projectile residue (GSR) patches aren't only emitted from the nib, but also from the spherical gaps,

ejection anchorages and other reflections present in the arm. These patches are a crucial piece of substantiation for forensic examinations. Imaging and assaying projectile residue (GSR) patches using the scanning electron microscopy with an energy dispersive spectroscopy (SEM/ EDX) (6) is a standard fashion that can give morphological and essential values of GSR patches present in the samples. Unfortunately, veritably many studies have been reported for the discovery of GSR patches for long distances using SEM. Therefore, In the present study, a new approach has applied to describe GSR patches for distant range firing by assaying the presence of Lead (Pb), Barium (Ba), Antimony (Sb) and other rudiments on the target material using SEM. (6) Results The targeted samples of the range, near contact to distant range from shooter have anatomized using the new approach by SEM and EDX. (6) The findings show the presence of GSR flyspeck indeed up to a distant range which is generally not detected from the conventional chemical and essential styles. Conclusions using this approach, it was possible to open an avenue in forensic disquisition to estimate the range between the target and a shooter for long distances (6). This system may be helpful to the forensic community and disquisition agencies to break the distant range of crime.

Projectile remainders (GSR) from an aggregate of nine different quality protections produced in Brazil were anatomized and characterized by transmission (TEM) and surveying electron microscopy (SEM). (7) GSR patches are composed of globular patches of several micrometres of periphery containing distinct quantities of lead, barium and antimony, along with other organic and inorganic rudiments arising from the manual, gunpowder, the gun and the pellet itself. This study was carried out to gain fresh information on the parcels of GSR nanoparticles began from different types of regular security produced in Brazil by CBC. Besides the SEM, we've used a TEM, exploring its high exaggeration capability and capability to explore internal structure and chemical

composition of submicron patches. We observed that CBC security generated lower patches than generally reported for other protections and that the three element patches aren't a maturity. TEM analysis revealed that GSR are incompletely composed of sub-micron patches as well. The electron diffraction pattern from these patches verified them to be substantially composed of lead oxides crystalline (7) nanoparticles that may be rolled into larger patches. Energy dispersive-ray spectroscopy revealed that utmost of them were composed of two rudiments, especially PbSb. Ba wasn't a common element set up in the nanoparticles. (7)

3D- printing is an arising fashion that enables the fast prototyping of multiple- use bias. Herein we report the fabrication of a 3D- published graphene/ polylactic acid (G- PLA) conductive electrode that works as a sample and a voltametric detector of essence in projectile residue (GSR) using a commercially-available G/- PLA hair. (8) The 3D- published face was used as tar to collect GSR and coming submitted to a square- surge voltametric checkup for the contemporaneous discovery of Pb²⁺ and Sb³⁺. The proposed detector presented excellent logical performance, with limit of discovery values of 0.5 and 1.8 $\mu\text{g L}^{-1}$ to Pb²⁺ and Sb³⁺, independently, and direct ranges between 50 and 1500 $\mu\text{g L}^{-1}$. slice was performed through the direct contact of G- PLA electrode in hands and clothes of shooters, (8) followed by absorption in the electrochemical cell in the presence of supporting electrolyte for the SWASV checkup. The proposed system showed a great performance in the recovery, identification and semi-quantification of Pb²⁺ and Sb³⁺ in the estimated samples without the need for sample medication. also, the device can be reused as sample and detector (until three times without loss of electrochemical performance) and the fabrication is reproducible (RSD = 7, for three different bias). Hence, this 3D- published material is an excellent seeker for the analysis of GSR (8), a necessary analysis in the forensic field.

Discovery and identification of organic and inorganic factors of projectile residue are well established within forensic chemistry because of largely characteristic and uncommon features of the products of security discharge at the time and place of a firing incident in comparison to other accoutrements present in diurnal life of people. Both types of residues play an important part in establishing colourful circumstances of a firing crime, though the most vital bone concerns the possibility of relating a suspect with the exertion of firing. In this aspect, solid, inorganic patches, currently called characteristic, have been employed. Their specific features affect from the manual admixture composition, including composites of heavy essence, lead, antimony, and barium, and from the extraordinarily dynamic conditions of their conformation, taking place at the moment of the manual eruption. Scanning electron microscopy and-ray microanalysis ways proved to be necessary and sufficient to reveal the content and the globular morphology of the patches for this purpose (9). lately, the recommendation that the eventuality for lead exposure be minimized was followed in the product of security cal. 9 mm Luger, 0.40 S&W, 0.380 bus, and 0.38 Special (9). These ultramodern types of security expel lower characteristic patches, the identification of which can be a challenge for the observers. At least two results to strengthen the residue identity are taken into account fresh perceptivity into the internal structure of inorganic patches., by means of electron backscattered diffraction and concentrated ion ray, as well as reciprocal examinations of organic remainders with sensitive mass spectrometric ways.

Projectile residue is emitted as fine particulate matter upon the ignition of percussion-sensitive snares among other complements in an arm barrel. The particulates condense from a vapor phase and contain material from the Pb- Sb- Ba- bearing manual, S-bearing gunpowder, and the Pb- bearing pellet fractions (10). Shooters can gobble or ingest the fine

particulates which also attach to their hands, apparel, and other shells. Estimation of the bioavailability of the emitted poisonous Pb- and Sb- bearing particulates requires detailed knowledge of their mineralogical composition and those of their riding products (10). For this purpose, projectile residue particulates have been collected from soils in front of a blasting line of a firing range in Ontario, Canada. Bulk mineralogical and chemical features of the soils have been characterized using-ray greasepaint diffraction, inductively coupled tube- mass spectrometry, and surveying electron microscopy. The focused ion- ray fashion has been used to prize a section containing multitudinous altered projectile residue particulates from a soil grain. posterior transmission electron microscopy shows for the first time that projectile residue particulates are composed of metallic δ - Pb, α - Sb, galena (PbS), and an unidentified Ba- bearing phase (10). Riding of the projectile residue particulates results in the conformation of incidental nanoparticles (i.e., not deliberately finagled to do at the nanometre scale) in the form of δ - Pb, massicot, PbO, and galena. The conformation and rallying of some of these nanoparticles within the soil grain suggest that their release during the riding of pellets and projectile residue contributes to the release of Pb into the terrain. Hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$, cerussite, PbCO_3 , and massicot and anglesite, PbSO_4 , are the major secondary Pb- phases in and around altered GSR particulates. These phases form during the riding of metallic Pb, massicot, and galena nanoparticles in a Ca- carbonate rich terrain. Secondary Sb- bearing phases are valentinite, Sb_2O_3 , and unformed Sb- Pb phases (SbPb rate = 21 – 41). The ultimate phases have incompletely replaced large proportions of the Ca-carbonates girding the projectile residue particulates. The larger cornucopia of the unformed Sb- Pb phases relative to valentinite suggests that their solubility most likely controls the release of Sb into the bulk soil. (10) The SEM and TEM characterizations and chemical analyses of mineral face coatings and the

colloidal bit of a leachate from the collected surficial soils indicate that Pb occurs generally in the colloidal bit, is frequently associated with sulphate-bearing colloids, and is sequestered in sulphate and carbonate/hydroxide coatings.

Electroanalysis of organic remainders of the fuel stabiliser ethyl-centralite (1,3 diethyl- 1,3 diphenyl urea, EC) (11) generated from the discharge of an armament or extemporized explosive bias is examined. relative goods of an electrode modifier, nanoparticles of magnetite (Fe₃O₄), on the detector performance was of interest, with customised published prototype development and analysis of organic arm residue (OFAR) samples. Differential palpitation voltammetry (DPV) estimation studies realised perceptivity of $6.37 \times 10^{-2} \mu\text{A} \cdot \mu\text{M}^{-1}$ (over the attention range $2.5 - 50 \mu\text{M}$) (11) at the glamorous nanoparticle modified electrode, representing a 1.65 fold signal increase relative to unmodified electrodes with limit of discovery $4.39 \mu\text{M}$. Addition of the OFARco-existing diphenylamine (DPA) stabiliser realised signal demarcation and perceptivity of 7.49×10^{-2} and $5.49 \times 10^{-2} \mu\text{A} \cdot \mu\text{M}^{-1}$ for DPA, and EC independently, (11) using DPV over the same range. The work crowned in the qualitative and quantitative analysis of fuel stabilisers in arm residue acquired from a single base shotgun shell, with recovery from a target sample cloth, together with unburnt fuel, making promising first way towards a customised screen-published prototype for use by forensic professionals. Scanning electron microscopy/ energy dispersive spectroscopy and infinitesimal force microscopy were employed for flyspeck confirmational analysis.

This study delved whether game meat may contain nanoparticles of lead from security. Lead nanoparticles (12) in the range 40 to 750 nm were detected by ICP-MS in single flyspeck mode in game shot with lead-containing pellets. The standard periphery of the detected nanoparticles was around 60 nm. The flyspeck mass attention ranged from 290 to 340 ng/ g meat and the flyspeck number attention

from 27 to 50 million patches/ g meat (12). The size limit of discovery explosively depended on the position of dissolved lead and was in the range of 40 to 80 nm. In game meat tried further than 10 cm down from the crack channel, no lead patches with a periphery larger than 40 nm were detected. In addition to dissolved lead in meat that began from particulates, the presence of lead nano patches in game meat represents a heretofore unattended source of lead with a largely unknown toxicological impact to humans.

The overall end of the work was to advance electrochemical bias able of analysis of forensically applicable remainders using rapid-fire electrochemical detector technology. In order to achieve this, electrochemical discovery of the fuel stabiliser diphenylamine (DPA) was achieved via voltammetry with signal improvement realised in the presence of iron oxide nanoparticle modified transducers. This allowed both mechanistic and logical evaluation with the end to achieve the needed selectivity and perceptivity for dependable discovery. DPA electrochemistry was examined at glassy carbon electrodes in waterless (37 methanol sodium acetate pH4.3) electrolyte via implicit broad, with an unrecoverable surge at $E_p = 0.67 \text{ V vs. Ag/ AgCl}$ (13). The prolixity measure (D) for the oxidation process was calculated as $1.43 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ with $\alpha n_a = 0.7$. DPA electrochemistry in a non-waterless methanol/ acetonitrile electrolyte redounded in a D value of $5.47 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ with $\alpha n_a = 0.5$. (13) Electrochemical medication of glamorous iron oxide nanoparticles was achieved via electrooxidation of an iron anode in the presence of an amine surfactant followed by characterisation with SEM/ EDX, XRD, FTIR and thermal analysis. A face confined subcaste of these glamorous nanoparticles served to appreciatively impact the response to DPA while impeding conformation of face confined oxidation products, with generation of a bettered logical signal-perceptivity $1.13 \times 10^{-3} \text{ A cm}^{-2} \text{ mM}^{-1}$ relative to bare electrode response ($9.80 \times 10^{-4} \text{ A cm}^{-2} \text{ mM}^{-1}$)

over the range 0.5 – 50 μM DPA using discriminational palpitation voltammetry, with $\text{LOD} 3.51 \times 10^{-6} \text{ M}$ and $\text{LOQ} 1.17 \times 10^{-5} \text{ M}$ (13). Real sample analysis involved recovery and discriminational palpitation voltammetry of unburnt and burnt projectile residue with DPA qualitative and quantitative analysis.

Inductively coupled tube mass spectrometry (ICP- MS) is an important tool for a rapid-fire analysis of chemical rudiments due to its high perceptivity, selectivity and multi-elemental character. Herein, the capability of the ICP- MS fashion is estimated to determine the projectile remainders (GSR) from clean range security using a 0.40 quality dynamo and a 0.38 quality revolver as a function of number of shots ($n = 1 - 7$ shots for the dynamo and $n = 1 - 5$ shots for the revolver) (15). The GSR was collected on the two regions of right and left hands thumb and forefinger win and thumb and forefinger back. ICP- MS results were compared to classical ways in the forensic ballistics the colorimetric test using sodium rhodizonate reagent and surveying electron microscope with energy dispersive X-ray spectrometry (SEM/ EDX). Negative results were set up for Pb and Ba using the colorimetric test from GSR with $n = 7$ shots from 0.40 quality dynamo (15). For SEM/ EDX analysis, photomicrographs show indefinite morphology for the GSR of clean range security, in discrepancy to report by conventional GSR. also, the EDX results primarily linked C, O, K, Al, S, Si, Cu, Zn, Ti, Cr, Cl, Mo, Sr, and Fe. Else, ICP- MS handed positive results for Pb, Ba and Sb, with maximum attention of $4.20 \mu\text{g} \cdot \text{L}^{-1}$, $10.9 \mu\text{g} \cdot \text{L}^{-1}$ and $0.119 \mu\text{g} \cdot \text{L}^{-1}$, independently, as well as for Al, Ti, Cr, Mo, Cu, Zn and Sr. Eventually, Al, Zn, Cu and Sr can be used as new labels of GSR of clean range security, since they're the most abundant species detected.

II. CONCLUSION

The article summarizes an introduction and different detection test for GSR and their effective results. There are many tests for detection of GSR but is very lengthy and time consuming. There is no such test which can tell us that suspected powder found is GSR on crime scene itself. Use of nanoparticle detection tells us that lead oxide is present in GSR which can be useful for further studies. In this article different test with help of nanoparticles is studied and results indicates the presences and study with nanoparticle is effectively possible. Further vast study can be carried forward in the same field.

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