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Spectroscopic involvement detection for Al^{3+} and Fe^{3+} ions through fluorescent probe in gunshot residue samples

Vidhun Sakthivel^a, Srinivasan Nagasundar^a, S. Monish Kumar^b, G. Prabakaran^b, Jeyaraj Prabhu^{b*} and Raju Nandhakumar^{b*}

^aDivision of Criminology and Forensic Science, Karunya Institute of Technology and Sciences, (Deemed-to-be University), Karunya Nagar, Coimbatore - 641 114, India.

^bFluorensic Materials Lab, Division of Physical Science, Karunya Institute of Technology and Sciences, (Deemed-to-be University), Karunya Nagar, Coimbatore - 641 114, India. E-mail: prabhuj@karunya.edu*

Abstract

A new way of detecting metal ions in gunshot residue (GSR) samples was carried out by using fluorescent chemosensor. The designed and synthesized chemosensor **R** was successfully characterized by NMR and mass spectroscopic techniques. The sensor **R** was synthesized by single step condensation method by taking 2-hydroxy-1-naphthaldehyde and naphthyl methyl amine. Sensor **R** successfully detects Al^{3+} and Fe^{3+} ions in both colorimetric and fluorimetric ways in DMSO- H_2O (1:1 (v/v), 50 mM, HEPES buffer, pH = 7.4) solutions. Although, **R** was treated with GSR samples which had series of metal ions confirmed through SEM-EDx data, it particularly detects Al^{3+} and Fe^{3+} ions in spectroscopic techniques. Before treating with GSR samples, sensor **R** emits very weak absorption and fluorescence emission which is due to C-N free rotation and keto-enol tautomerism. Upon treating with GSR samples, in colorimetric method it detects Fe^{3+} ions and Al^{3+} ions in fluorimetric method, C-N free rotation and keto-enol tautomerism is restricted and there occurs the change in absorption and fluorescence emission. At the present stage, sensor **R** could acts as a fluorescence agent in forensic applications for the detection of metal ions.

1. Introduction

Gun powder or black powder. To produce black powder a specific measure of nitrate (KNO_3) sulphur (S) and charcoal (C) must be combined with precision [1–4]. It is generally agreed upon that gunpowder and weapons originated in ancient China. It is widely assumed that alchemists in the medieval period discovered the fact that mixes of nitrate, sulphur, and charcoal ignite and explode during alchemy practice no later than the Tang Dynasty period [5,6]. The proliferation of missile propulsion was forever changed by the development of black powder - an amalgam made up of potassium nitrate combined with charcoal and sulphur which dramatically altered the course of warfare. Its first recorded use was in China and India during the eleventh century when it was employed for pyrotechnic displays or used as an incendiary agent; a practice that soon became commonplace [7]. The present day recipe for black powder typically comprises 75% saltpetre, 15% charcoal, and 10% sulphur but variations exist in purity levels along with alternative ratios. Scientists are still uncertain about many details concerning black powder's past such as who first conceived it or when it started being utilized in missile propulsion technology [8,9]. Nonetheless there is no disputing that this invention had a profound influence on technological advancements involving missile propulsion technology - transforming warfare forevermore [10,11]. Roger Bacon was an English Franciscan monk who made history in 1249 by identifying and describing the constituents of black powder—potassium nitrate (saltpetre) charcoal, and sulphur. Interestingly enough he didn't utilize this mixture for launching projectiles out of firearms; that credit goes to a German Franciscan friar named Berthold Schwartz who used it for that very purpose during the early 14th century. Black powder was once referred to as "gunpowder," serving as the propellant for firearms for many years [12]. However this explosive substance faced some challenges early on. Gunpowder tended to separate into components when transported and easily absorbed moisture - making it an unreliable option. Moreover variability in constituent purity only added another layer of uncertainty.

The chemical reaction initiated by firing pins striking percussion caps produces an expansion plume that releases vaporized primer- and bullet derived compounds into the air as particles that cool down over time to become what we know today as GSR evidence [13,14]. The substance known as gunshot residue has become a key focus in the realm of forensic science. Its other names - firearm discharge residue and cartridge discharge residue - underscore its significance in cases involving firearms and weapons [15]. Efficiently analysing gunshot residue (GSR) is one essential aspect of forensic sciences toolkit - particularly for reconstructing firearms offenses accurately. GSR is made up mostly of partially burned gunpowder, combustion products and various other particles derived from bullets themselves as well as cartridges or

weapons used in general. In this article, we'll take an in depth look at how GSR behaves and how it's detected through extensive research literature review. We will also pay particular attention to interpreting transfer patterns within real world casework scenarios. Forensic scientists often rely on identifying gunshot residue (GSR) found on clothing when investigating shooting incidents. In this study researchers used an experimental approach together with SEM-EDx analysis to determine whether washing clothes worn while firing a 0.22 rifle would affect GSR identification and analysis under conditions similar to those encountered during forensic investigations [16]. Of significance to law enforcement officials is that analysing GSR can help pinpoint individuals potentially linked with a shooting incident by detecting its presence on their clothing after washing. Using SEM-EDx analysis to decipher its chemical composition provides valuable information about details surrounding each case like weapon type used, firing distance and shooter position.

In forensic science investigations involving firearms-related crimes, proper sampling techniques are critical for obtaining reliable results. The specific location that sample collections take place depends on multiple factors such as the type and location of the crime committed - be it a homicide or suicide case [17]. For example, vehicular sites like seats and headlights may be sampled alongside body regions like clothing worn by victims or suspects. To ensure accuracy in analysis of GSR sample collections must be done efficiently since residue particles begin degrading shortly after weapon discharge - usually within two hours leading to difficulty in detection sensitivity later on [18]. Depending on whether organic or inorganic traces are detected at the SOC there are different collection method options available: dry methods using molten wax or adhesive tapes compared to wet techniques employing diluted acetic acid or hydrochloric acid solutions. When collecting as much particulate matter as possible from a shot residue sample, it's crucial to implement the most fitting technique. Detection and analysis of inorganic residues require a bulk analytical technique capable of handling multiple elements; hence commonly used methods include NAA, ICP, AAS and SEM/EDx [4]. While laboratory testing traditionally focused on detecting these types of residues; progressively more scientists have begun investigating organic compounds from firearm propellants in GSR's by utilizing advanced techniques such as Gas Chromatography mass spectrometry, High performance liquid chromatography, Capillary electrophoresis, Raman spectroscopy and thin layer chromatography [3,19-23].

1.2 Components of gunshot residue

When a firearm is discharged it leaves behind a residue made up of both organic and inorganic components. Propellants and lubricants contribute to organic residues while primers, propellants casing material as well as jacket cores make up the inorganic constituents. The range particle size varies between reports with a range between 0.5 - 10µm or more [24]. Forensic Scientists can analyse this residue by examining particles formed when vaporized materials solidify into distinct sizes. The use of black powder has become obsolete; it has since been replaced by smokeless powder which consists mostly of nitroglycerine alongside other single- or double base powders as well as various lubricants, additives, coolants, inhibitors, plasticizers etcetera. Manufacturers create different compositions for their primers' inorganic ingredients hence formulation varies. However modern day formulations include a combination of lead styphnate, barium nitrate and antimony trisulfate which first appeared in 1921. Inorganic constituents such as lead [25], antimony, barium [26], Zinc, Sodium nitrate [27], Mercury, potassium, magnesium, Aluminum [28] are used for the source of primer. Organic constituents such as Nitroglycerine, Nitrocellulose are also used as a source for primer mixture. Diphenylamine (DPA) Ethyl centralite(EC), Ethyl phthalates, Glyceryl triacetate, 2,6-Dinitrotoluene (DNT), Nitro guanidine, 2,4,6-Trinitrotoluene, Akardite II (AK II), Methyl centralite (N, N-dimethyl carbanilide), Cyclonite (RDX) and chromium, Nitrites were used as propellants.

1.3 Recent development in GSR detection:

1.3.1 Advancement in presumptive test

In forensic ballistics, gunshot residue (GSR) particles can be detected using screening or presumptive tests which are mainly focused on the chromophoric reaction. Most tests serve as an initial indication for a forensic investigator at the crime scene before instrumental analysis for definitive identification. The screening methods are known to be convenient, have fast analysis, and minimal preparation. In recent years, the focus in forensic investigation has shifted towards portable and fast methods that can be performed in-situ rather than in an analytical laboratory. Unfortunately, the current technique for detecting GSR cannot provide fast detection at a crime scene. The screening method is an essential technique in forensic analysis that can minimize the time taken to analyse data. This technique can be achieved if the screening and confirmatory methods can be done at the crime scene. Most forensic analysts apply the use of color changes in order to determine the presence of nitro groups or heavy metals in GSR particles [20,29]. Part of investigating crime scenes involves detecting GSR on clothing or hands of potential shooters effectively. This study was to find a novel technique to detect and perform screening tests is through using the Rapid Griess Test (RGT) reagent instead of traditional means like Modified Griess Test (MGT) analysis which has some similarity with results obtained through RGT tests only with some differences in color intensity. RGT reagents' effectiveness eliminates the need to heat and use acetic acid for chromophoric reactions, making it a more efficient method. Substituting the traditional MGT with RGT as a screening

technique to detect NO₂ as GSR's primary composition can create new opportunities in forensic chemistry analysis [30,31]. However, this approach is subject to the availability of samples collected from the crime scene immediately.

1.3.2 Use of luminescent marker in GSR detection

Scientists have found a successful alternative by inserting various luminescent markers into ammunition; Ln-MOFs show particularly promising results as one such material and are expanding forensic ballistics research opportunities [32,33]. By testing combinations of Ln-MOFs synthetically added to ammo, researchers can visualize LGSR on-site using these trusted markers' unique properties. Not only does lanthanide aid in characterizing LGSR but it also allows for selective marking of ammunition with conventional ammo increasing both analysis accuracy as well as collection efficiency - while being less toxic & more cost-effective making it an ideal option [27,34,35]. To perform thorough analysis, it is crucial to have a standard protocol for LGSR analysis that incorporates various techniques. Looking ahead, testing the compatibility of different Ln-MOFs combinations with forensic phenomena has the potential to benefit the entire forensic community.

A study was proposed on electrochemical methods with disposable screen-printed carbon electrodes for GSR screening at the laboratory and points of care due to their rapid, cost-efficient, and compact platform. GSR residues were extracted from typical aluminum/carbon adhesive collection stubs and analyzed via square-wave anodic stripping voltammetry. Bench top and portable electrochemical instruments were compared for the assessment and classification of authentic shooter samples by monitoring a panel of inorganic and organic GSR elements and compounds including lead, antimony, copper, 2,4-dinitrotoluene, diphenylamine, nitroglycerin, and ethyl centralite. The evaluation included the assessment of figures of merit and performance measures from quality controls, non-shooter, and shooter data sets. Samples collected from the hands of 200 background individuals (non-shooters), and shooters who fired leaded ammunition (100) and lead-free ammunition (50) were analyzed by the benchtop and portable systems with accuracies of 95.7% and 96.5%, respectively. The findings indicate that electrochemical methods are fast, sensitive, and specific for the identification of inorganic and organic gunshot residues. The portable potentiostat provided results comparable with the benchtop system, serving as a proof-of-concept to transition this methodology to crime scenes for a practical and inexpensive GSR screening that could reduce backlogs, improve investigative leads. In this study it has been demonstrated that gunshot residue can be detected after harsh treatments such as washing through SEM-EDS and a novel method on specific detection of Fe³⁺ and Al³⁺ ions gunshot residue has been successfully carried out using fluorescent chemosensor (R)

2. Experimental section

2.1 Materials and Methods

2.1.1 Pre examination:

A white lab coat was purchased from saberwal scientific company. The coat was initially cleaned, dried, and utilized for this investigation in order to remove the undesirable particles from the material. UV and visible lights are passed to check for any undesired particles, and the coat was then packed in a zip lock polythene bag.

2.1.2 Weather conditions:

Temperature - 22 °C; Barometer: 1014 mbar; Wind speed - 13 km/h; Humidity - 50 % (Fig.1a).

2.1.3 Specification of Sporting rifle 0.22:

Total length of the gun - 43 inches ; Barrel length - 632 mm ;Weight - 6lbs ; Caliber - .22 inch LR; Chamber- International standard LR (5.70 mm x 16.50 mm); Grooves - 6 no's R.H. 1 turn in 200 mm; Range - 200 m max ; Safety - on rear end top of the body by turning lever safety ; Trigger pull - Adjustable (min 1kg); Furniture - wooden ; Magazine capacity - 10 rounds ; Effective range - 75 ft ; Ammunition - Rimfire ; Muzzle velocity - 1,120–1,135 ft/s (Fig. 1b).

2.1.4 Condition for firing:

The candidate who is firing was free of any kind of metal so that there won't be any transfer of metals to the sampling material. The candidate fires the gun ½ feet limber up lying position over dhari (carpet) in order to acquire stability while shooting , a helper is provided for loading of bullets in the gun (Fig. 1c).

2.2 Real time experiment

Step one:

An experiment was conducted outdoors using targets placed at a distance of 50 meters. The shooter, who was wearing a lab coat, fired 21 rounds while lying down (Fig. 1d). To prevent secondary transfer of gunshot residue (GSR) from one part of the coat to another, the coat was collected in a plastic bag using long tongs by a helper wearing gloves. The coat was then folded, with paper in between each fold (Fig. 1e).

Step two:

The coat was soaked in liquid detergent for 30 minutes (Fig. 1f), it was hand-washed using a cloth brush with the **five-outward-stroke** method, and then the process was repeated after flipping the coat upside down. Cleaned under running water, and dried in an enclosed space using a fan.

Step three:

A hand vacuum (800 W, high power) with the same lab coat material attached to its mouth to exactly fit so that the vacuumed GSR would get trapped in it. They were systematically vacuumed (grid pattern) to collect all the GSR content from the coat, which was then captured on the same material fitted inside the vacuum (Fig. 1g).

Step four:

The sample was then viewed under the microscope for any deposition of GSR over it as a preliminary examination. It was observed that there was some kind of deposition on the sample material (Fig. 1h). For further analysis, the material sample is taken for SEM and EDX examination (Carl Zeiss Sigma 300 FESEM with smart edx detector made in Germany) (Fig. 1i).

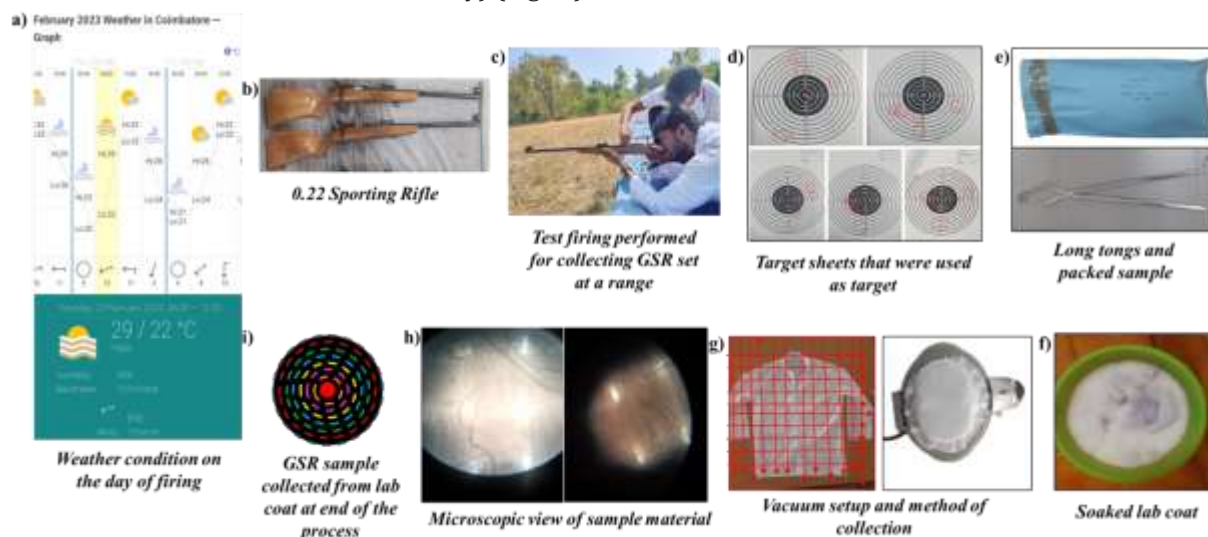


Fig. 1. Experimental set-up for the making of GSR sample

3. Results and Discussion

3.1 Characterization of GSR sample in scanning electron microscope

As shown in the Fig. 2, SEM image of a typical “unique particle” obtained from all the 21 rounds of the 0.22 rifle. Typically, the GSR samples possess regular or distorted spherical-like shape. Occasionally, objects similar to sponge fragments or spherical shell fragments and spherical aggregates of various sizes were also observed. The particle shown in Fig.2a was $\sim 200\ \mu\text{m}$ in diameter, followed by different nanometre from $100\ \mu\text{m} - 2\ \mu\text{m}$ (Fig. 2b-f). The range of dimensions of GSR particles ($1-100\ \mu\text{m}$) distinguished GSR from the environmental solid particles ($>100\ \mu\text{m}$) The GSR particles detected in the collected samples were classified based on their elemental content.

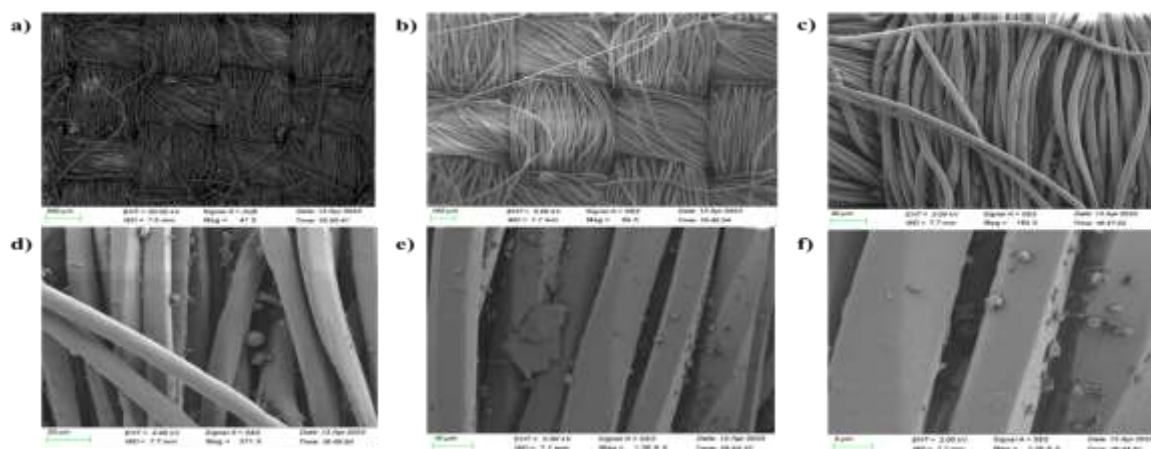


Fig. 2. The obtained GSR sample viewed at different nanometre using scanning electron microscope a) 200µm b) 100µm c) 50µm d) 20µm e) 10µm f) 5µm.

3.2 Characterization of GSR sample in SEM-EDx analysis

As shown in the Fig. 3, GSR sample was recorded in SEM-EDx spectrum of the unique spots. The spectrum clearly showed the characteristic elements Sb, Ba and Pb. The presence of unique particles with characteristic elements indicated that this sample was gathered from the shooter's garment. The EDx spectrum from different spots shows the elements found in GSR particles collected. Upon the spectrum results, the mainly obtained elements were C, Ca, O, Pb, Cl, Sb, As, Al, Ba and Fe ions. Al, Cu, K and Si originated from the primer mixture. N, C and O corresponded to the nitrocellulose. Presence of Al, Ni, Cu and Zn can be attributed to the bullet, cartridge case, metal jacket and bullet coating as they were usually made of brass (70% Cu: 30% Zn). Low intensity signals of Ca, Cl, S and Ti elements were also detected. The results from SEM-EDx of collected GSR sample showed the morphological structure changes and presence of elements and ions in gunshot residue as shown in the images collected from the different spots from spot 1 to 3 as shown in (Fig. 3a-h) and the concentration of each element are shown in (Table. S1-S4).

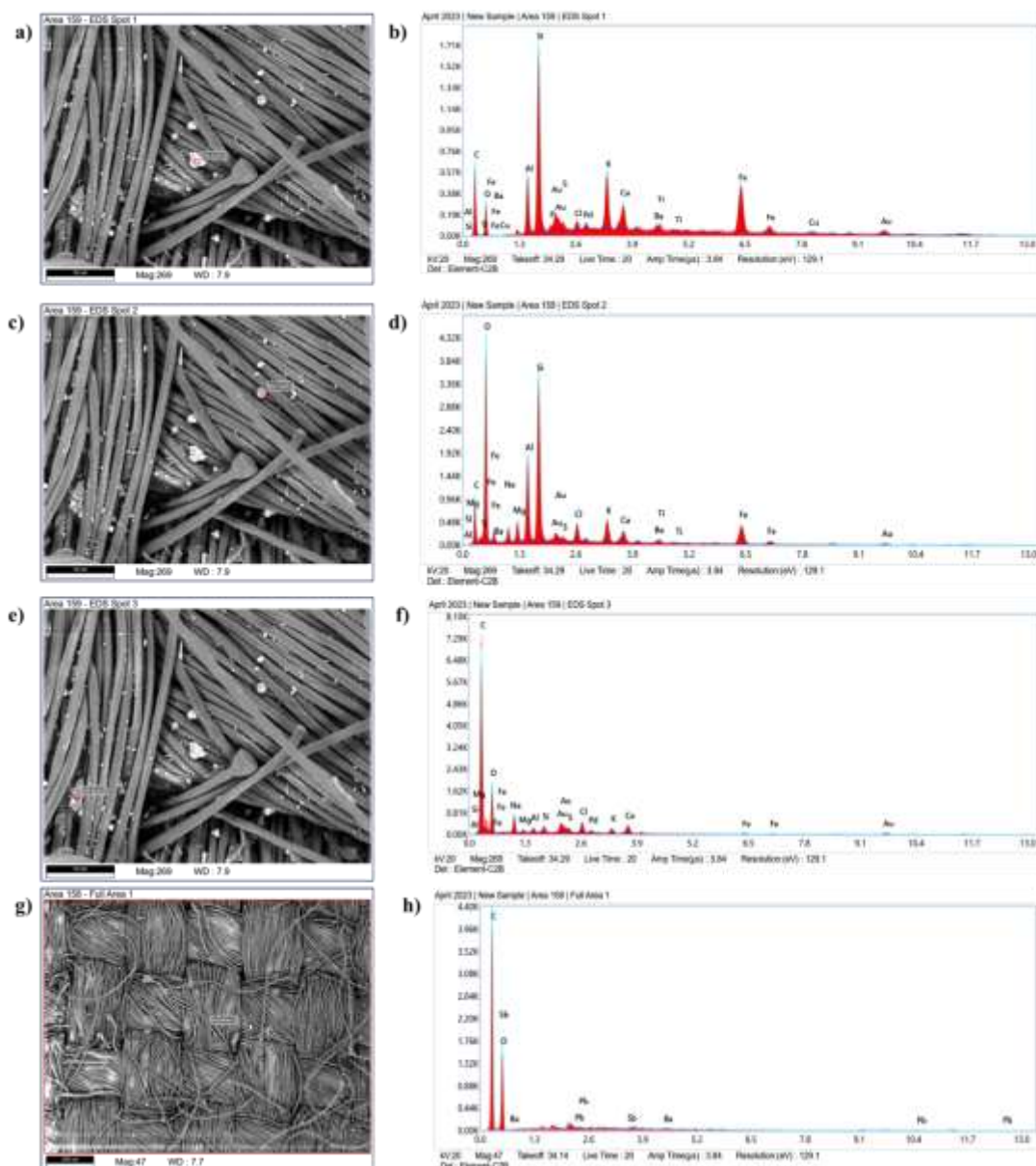


Fig. 3. SEM-EDx analysis of GSR samples collected from different spots.

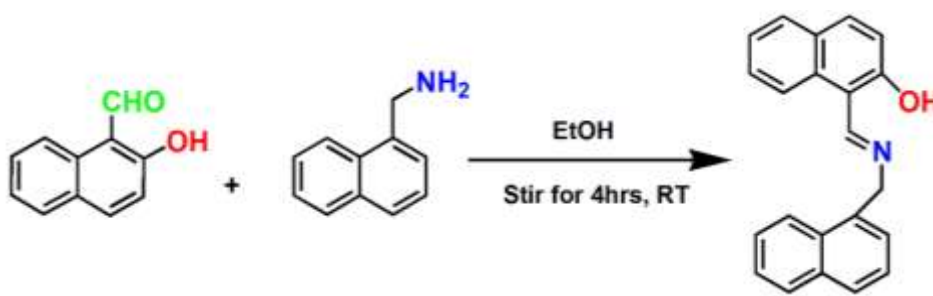
3.3 Detection of Al^{3+} and Fe^{3+} ions in GSR sample through chemosensor R

3.3.1 Chemosensor R

Upon the confirmation from microscopic and spectroscopic techniques, the presence of Al^{3+} and Fe^{3+} ions are identified in GSR sample. So here we used a chemosensor (**R**) for the detection of both ions in colorimetric and fluorimetric ways. Sensor **R** have been already examined against different environmental and biological metal ions DMSO- H_2O (1:1 (v/v), 50 mM, HEPES buffer, pH = 7.4) solution [36]. In that way, sensor **R** selectively detects Al^{3+} ion in fluorimetry and Fe^{3+} ion in colorimetry present in GSR samples.

The design of chemosensor **R** takes through a simple schiff base reaction by condensing 2-hydroxy-1-naphthaldehyde and naphthyl methyl amine in 25ml of ethanol for 4 hours under room temperature. The final product was obtained by keeping the crude for slow evaporation in room temperature to get yellow

precipitate. The final crude was characterized by ^1H NMR, ^{13}C NMR and LC-MS spectroscopic techniques (Fig. S1-S3). As shown in scheme 1, the obtained sensor **R** was used for detecting Al^{3+} and Fe^{3+} ions in GSR sample obtained from lab coat.



Scheme. 1. Design and construction of Chemosensor **R**

3.3.2 Colorimetric detection of Fe^{3+} ions in GSR sample

The purpose of the designed chemosensor **R** was to detect the metal ions in practical applications. Upon that, here the sensor **R** was used for the specific sensing of Fe^{3+} ions in collected GSR samples. From the SEM-EDx preliminary results, it's evident that the present of Fe^{3+} ions in GSR samples. As reported earlier, sensor **R** could detect Fe^{3+} ions in DMSO- H_2O (1:1 (v/v), 50 mM, HEPES buffer, pH = 7.4) solution. So here, the collected GSR samples were diluted to 10ml of DI water, neutralized to pH = 7.4 and treated against sensor **R**. From the Fig, it's very clear that sensor **R** detects Fe^{3+} ions in GSR sample with the presence of other metal ions. Here, sensor **R** had weak absorption emission before treating with metal ions. Upon addition of metal ions and GSR sample, sensor **R** binds specifically Fe^{3+} ions in presence of other metal ions which also provided a depth results that there's no interference of other metal ions. These results propose that, sensor **R** could acts as a fluorescence agent for the detection of Fe^{3+} ions in gunshot residue (GSR) sample, which could play a prominent role in forensic applications.

3.3.3 Fluorimetric detection of Al^{3+} ions in GSR sample

On the other hand, fluorimetric detection of chemosensor **R** was examined against GSR sample with the same procedure followed for colorimetric detection. Collected GSR sample was diluted to fluorimetric concentration and later neutralized to pH range of 7.4. As reported earlier, sensor **R** detects Al^{3+} ions in fluorimetric detection in DMSO- H_2O (1:1 (v/v), 50 mM, HEPES buffer, pH = 7.4) solution. So, GSR sample which was found to have Al ions was tested against sensor **R**. From the fig, sensor **R** had weak fluorescence intensity, when **R** is treated with different metal ions, Al^{3+} only showed fluorescence activity with enhancement in intensity. So here, we examined collected GSR sample with sensor **R**, were we found more or less same kind of fluorescence intensity with enhancement was observed. From these results, it provided a clear spectroscopic evidence for the detection of Fe and Al ions in GSR sample through DMSO- H_2O (1:1 (v/v), 50 mM, HEPES buffer, pH = 7.4) solutions.

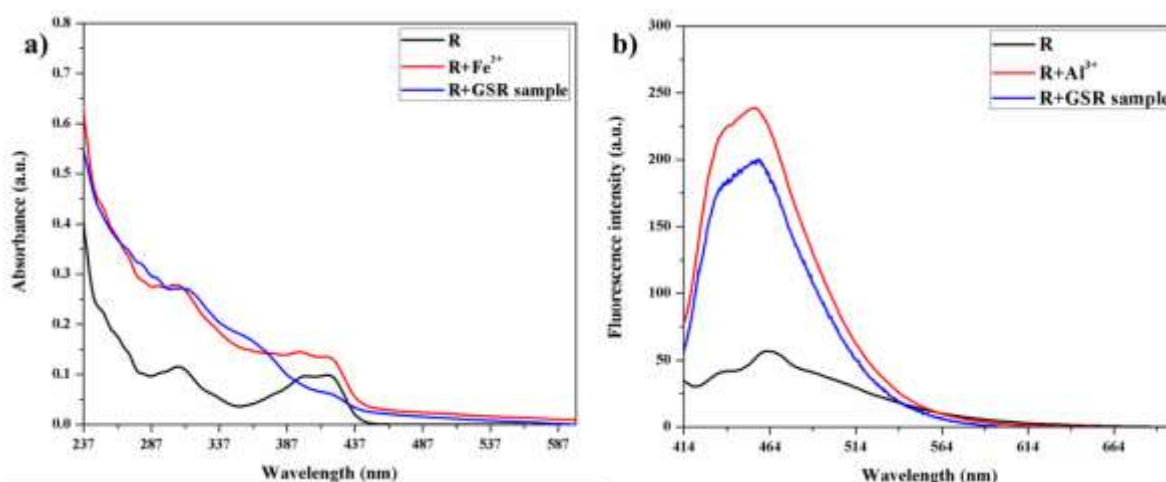


Fig. 4. a) Colorimetric detection of sensor **R** in presence of Fe^{3+} ions and GSR sample. b) Fluorimetric detection of sensor **R** in presence of Al^{3+} ions and GSR sample in DMSO- H_2O (1:1 (v/v), 50 mM, HEPES buffer, pH = 7.4) solutions.

4. Binding mode

4.1 Plausible binding mode of GSR sample for the detection of Al and Fe ions in colorimetric and fluorimetric ways.

Based on the spectroscopic techniques, possible binding mechanism was purposed for the detection of Al and Fe ions for GSR samples. Both the metal ions, binds with sensor **R** due to the presence of $-\text{OH}$ moiety

presence. As a free sensor, R had very weak absorption emission and fluorescence intensity which is mainly due to C-N free rotation and keto-enol tautomerism. Upon the examination of GSR samples towards sensor R, free rotation restricted and binding of metal ions takes place in C-N of nitrogen and -OH moiety which changes the absorption emission increment and enhancement in fluorescence intensity. From these evidences, sensor R could play an important role in detection of metal ions in GSR samples and also sensor R may be a useful fluorescent organic molecule (FOM) in forensic applications.

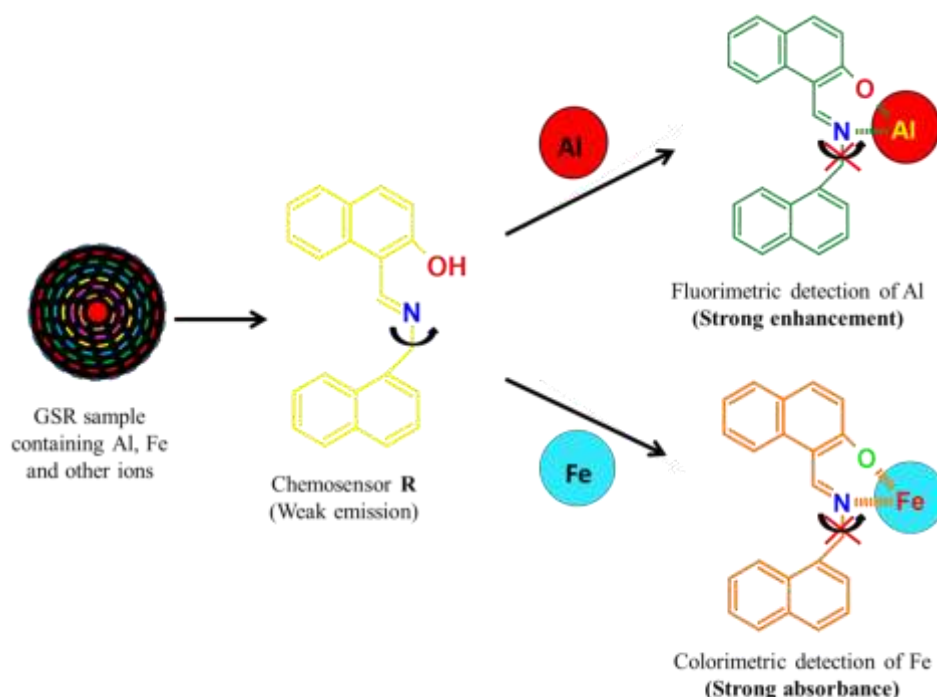


Fig. 5. Possible binding mechanism of sensor R for the detection of metal ions in GSR samples.

5. Conclusion

This research study has significant implications for forensic science applications in criminal cases. By analysing GSR particles found in connection with firearm related incidents crucial evidence is provided which allows authorities to identify perpetrators leading to successful prosecutions. Advanced analytic techniques such as SEM EDS technology coupled with chemosensor that detects Al^{3+} and Fe^{3+} ions provide more accurate results which create stronger trial evidence that can withstand scrutiny in court proceedings. It is essential to note though this research shows limitations when used alone to determine guilt or innocence; other aspects such as ballistics analysis coupled with witness statements must also be considered before coming to conclusions. In addition there are cases where discovered GSR particles on clothing do not automatically connect an individual directly firing a weapon as other factors might result in their presence at a crime scene location. In summary, identifying particles from discharging weapons using new technology like SEM-EDx and chemosensors detecting Al^{3+} and Fe^{3+} ions on shooters' cleaned clothing can provide a valuable resource in forensic science methodology. Gunshot Residue (GSR) found on a suspect's clothing can provide valuable leads for investigators working on a shooting case. Yet, it is equally important to remember that other pieces of evidence must be weighed and considered before reaching any decisive conclusions during criminal investigations.

Credit authorship contribution statement

Vidhun Sakthivel: Writing – review & editing, Formal analysis, Writing – original draft. Srinivasan Nagasundar: Writing – original draft, Data curation. S. Monish kumar: Conceptualization, Writing – review & editing, Formal analysis, Writing – original draft, Data curation. G. Prabakaran: Conceptualization, Writing – review & editing, Formal analysis, Writing – original draft, Data curation. Jeyaraj Prabhu: Writing – review & editing, Formal analysis, Writing – original draft. Raju Nandhakumar: Conceptualization, Writing – review & editing, Formal analysis, Writing – original draft, Data curation, Project administration, Funding acquisition.

NOTES

The authors declare no competing financial interest.

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Table. S1. EDS data of spot 1

Element	Weight (%)	Atomic (%)	Error (%)	Net Int.	R	A	F
C K	25.78	51.95	13.04	130.97	0.8404	0.0549	1.0000
O K	10.06	15.21	12.97	93.37	0.8545	0.0786	1.0000
Al K	4.43	3.98	8.51	217.41	0.8816	0.4619	1.0093
Si K	12.64	10.89	6.45	713.60	0.8864	0.5510	1.0090
P K	0.47	0.37	22.32	20.56	0.8910	0.5708	1.0139
S K	0.80	0.60	17.13	36.06	0.8953	0.6050	1.0156
Cl K	0.97	0.66	17.14	41.85	0.8996	0.6664	1.0212
K K	7.12	4.41	6.49	283.33	0.9078	0.7722	1.0288
Ca K	3.82	2.31	8.85	131.84	0.9118	0.7907	1.0325

Ti K	0.63	0.32	30.69	20.32	0.9196	0.8604	1.0588
Fe K	14.99	6.50	4.59	315.48	0.9349	0.9401	1.0702
Cu K	1.17	0.45	39.76	16.47	0.9470	0.9541	1.1325
Pd L	1.27	0.29	31.60	27.18	0.9043	0.7075	1.0084
Ba L	2.34	0.41	41.83	26.46	0.9233	0.8718	1.0197
Au L	13.51	1.66	27.13	39.85	0.9707	0.9805	1.0334

Table. S2. EDS data of spot 2

Element	Weight (%)	Atomic (%)	Error (%)	Net Int.	R	A	F
C K	17.85	28.48	12.92	191.23	0.8898	0.0521	1.0000
O K	41.34	49.52	10.36	1306.39	0.9015	0.1208	1.0000
Na K	2.16	1.80	12.14	111.88	0.9150	0.2421	1.0036
Mg K	1.83	1.44	10.11	166.93	0.9191	0.3623	1.0059
Al K	6.48	4.61	7.20	734.11	0.9230	0.4844	1.0077
Si K	11.69	7.98	6.06	1474.69	0.9267	0.5603	1.0061
S K	0.35	0.21	18.96	37.95	0.9335	0.6605	1.0128
Cl K	1.82	0.98	7.59	188.06	0.9366	0.7324	1.0163
K K	2.80	1.37	6.00	262.61	0.9427	0.8335	1.0255
Ca K	1.71	0.82	7.93	140.20	0.9457	0.8611	1.0293
Ti K	0.31	0.12	26.22	23.20	0.9512	0.9137	1.0528
Fe K	6.02	2.07	4.47	284.97	0.9618	0.9663	1.0727
Ba L	1.07	0.15	37.69	27.98	0.9539	0.9215	1.0161
Au L	4.57	0.45	30.33	29.76	0.9838	0.9913	1.0424

Table. S3. EDS data of spot 3

Element	Weight (%)	Atomic (%)	Error (%)	Net Int.	R	A	F
C K	49.84	64.65	11.00	964.40	0.9033	0.1005	1.0000
O K	28.72	27.97	11.38	554.95	0.9140	0.0790	1.0000
Na K	4.42	3.00	10.32	246.19	0.9263	0.2791	1.0026
Mg K	0.43	0.28	16.31	39.66	0.9300	0.3919	1.0040
Al K	0.64	0.37	11.49	73.77	0.9336	0.5257	1.0064
Si K	0.76	0.42	10.48	102.82	0.9369	0.6411	1.0091
S K	0.72	0.35	10.51	83.80	0.9430	0.7575	1.0145
Cl K	1.81	0.80	7.61	190.83	0.9458	0.7985	1.0167
K K	1.06	0.42	11.93	96.10	0.9513	0.8630	1.0264
Ca K	2.20	0.85	6.13	173.72	0.9539	0.8885	1.0264
Fe K	0.53	0.15	18.19	24.60	0.9681	0.9737	1.1251
Pd L	0.62	0.09	27.14	31.34	0.9490	0.8187	1.0058
Au L	8.24	0.65	20.46	50.48	0.9868	0.9948	1.0486

Table. S4. EDS data of full area

Element	Weight (%)	Atomic (%)	Error (%)	Net Int.	R	A	F
C K	58.55	66.53	9.80	1278.19	0.9308	0.1716	1.0000
O K	38.95	33.23	11.12	536.57	0.9392	0.0854	1.0000
Sb L	1.09	0.12	32.78	27.32	0.9703	0.9576	1.0093
Ba L	0.76	0.08	48.63	12.73	0.9746	0.9752	1.0135
Pb M	0.65	0.04	13.17	21.44	0.9623	0.8606	1.0056

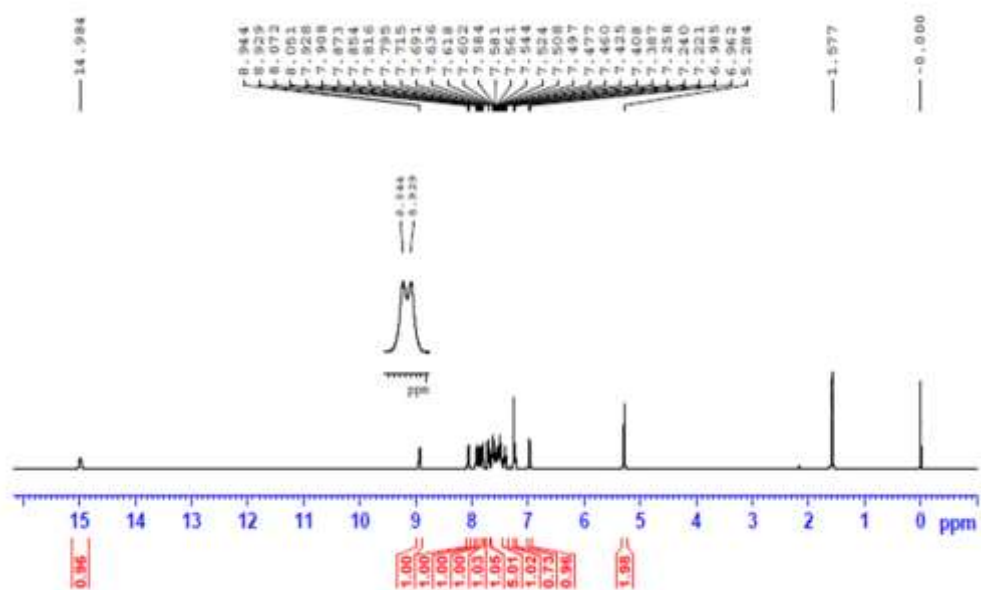


Figure. S1. ^1H NMR Spectrum of sensor R

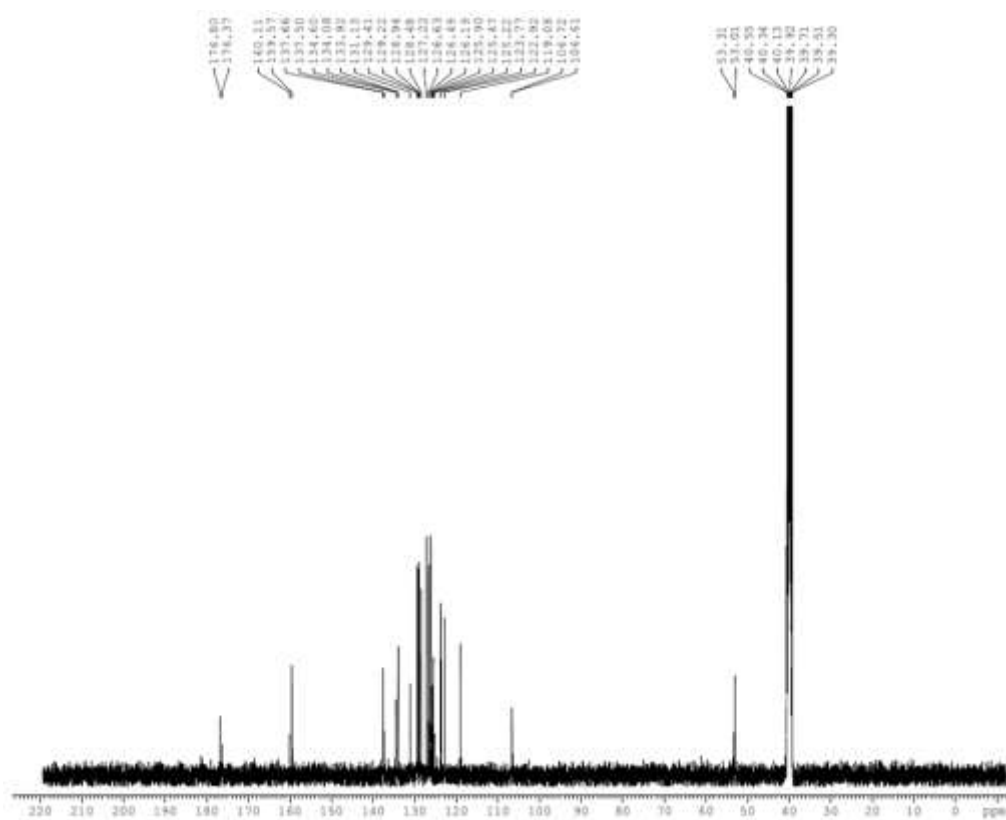


Figure. S2. ^{13}C NMR Spectrum of sensor R

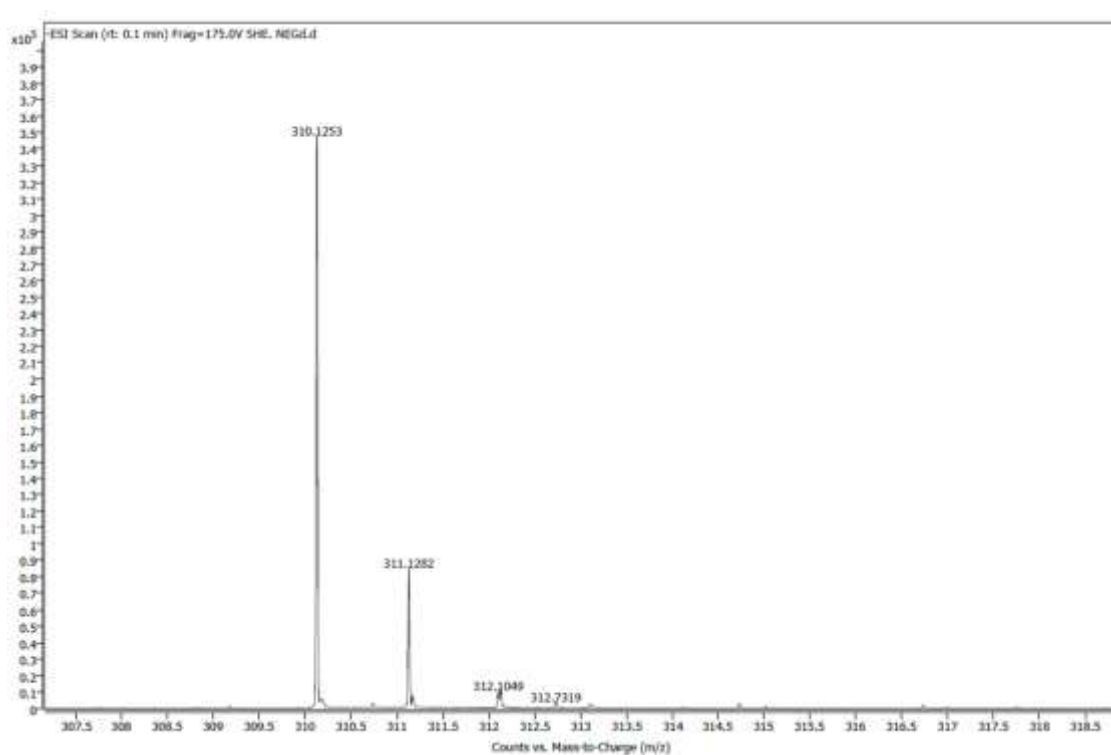


Figure. S3. Mass Spectrum of sensor R