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Trace Metal Detection of Inorganic Gun-Shot Residue of 5.32 INSAS Firearms using ICP-OES and Statistical Approach

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Abstract:- Gunshot residues is important analysis for identifying the type of firearms and ammunitions. Organic residues fades away and inorganic residues is next analytical possibility like lead free bullets. The major challenge is detection with non-destructive analysis due to trace levels and destructive analysis like acid digestion coupled inductively coupled optical emission spectroscopy able to detect trace levels from bullet casing, firearms and explosives during the shots. This was experimented with firearms of INSAS and 5.56 mm ammunitions in various distances from 0 to 300 cm fired with single shot. The GSR substrate collected, stored and analysed for visual photography to understand the bullet hole intact. The analysis found the average hole diameter was 1.22 ± 0.16 mm via photography, which was similar to other firearms. The gun powder and GSR substrate elements has no relation due to matrice non-corrected for ammunition. Still, the study succeeded by correcting the matrices of GSR substrate found with the help of statistical approach (Spearman correlation and principal component analysis). The possible signature for this ammunition were Pb, Cu, Fe, Ni, Zn, Ba, B, Sr, Ti, Mn and Al. Cu and Pb was observed upto 120 and 60 cm with possible trend on distances fired. Using Pb and Cu ratios the distance was regressed upto 62 and 63% for both matrices approach upto 105 cm. In the real scenario, collecting the substrate away from GSR might be useful for matrice correction in ballistics distance approximation.

Keywords: GSR, 5.56 mm, INSAS, ICP-OES, Lead-Copper

1. Introduction

Majorly, gunshot residues (GSR) contains both organic and inorganic deposits due to the composition from the rim fire primer mix materials on primary explosives, oxidising agent and fuel source. Apart from this, the small trace amounts of inorganic residues comes from barrels, bullets and casing due to the fire explosion occurred in these metals to leach. Thereby, the residues will contain both the mixtures. Organic residues have limited time to identify the residues from the samples and need to be analysed quickly either in the mass spectrometry or infrared spectroscopy or Raman spectroscopy. The another major problem in organic residue is difficultly in analysis due to the matrix complexity of the samples and degrading time of the organic compound is quicker. This leading the samples need to be extracted with organic solvents. But in today's world use of metal free explosives are available and worry some of identification difficulty in forensic applications [1–3].

Similarly, inorganic residues will be present in the form metal elements either in oxides or nitrates or sulphates. Other than the high-level explosions occur in the barrels, bullets and casing, there are chances of trace levels of metal contamination due to the natural existence in the samples are found along with the residues. This will make

even difficult to identify the type of ammunitions and firearms used in the crime for matching or not. Thereby, the researchers have used the chemical fingerprints of the bullet powders such as lead (Pb), barium (Ba) and antimony (Sb) are used in explosives, oxidising agent and fuel source. Which in the form of lead styphnate, barium nitrate and antimony sulphide respectively. However, researchers are reported the other forms of inorganic elements like tin (Sn), aluminium (Al), cadmium (Cd), arsenic (As), copper (Cu), bismuth (Bi), silver (Ag), titanium (Ti), magnesium (Mg) and iron (Fe) made for replacement of lead in the explosives. This makes the forensic analysis need to be carried out in multi-elemental in single run, as evidence is very low in mass or volume to detect the trace levels of inorganic residues [4–9].

In single run, the samples are able to analysis in two ways by non-destructive and destructive method. The non-destructive analysis by scanning electron microscope with energy dispersive X-ray spectrum (SEM EDAS) and X-ray fluorimeter (XRF). For the destructive analysis such as neutron activation analysis (NAA), atomic absorption spectrometry (AAS), inductively coupled plasma optical emission and mass spectrometry (ICP-OES and ICP-MS). The major differences between them are detection limit is too high for the non-destructive and time-consuming chemical process in destructive analysis. This makes the researchers need to be heavily relied on the non-destructive method for the forensic measurement due to faster analysis not with trace evidence. There are chances of cross interferences like d-block metal possible in the X-ray dispersion or fluorimeter such as Lβ of Pb at 10,550 eV can able to interfere with Kα of As 10,543 eV based on the X-ray emissions. Similarly, Lβ of Sb at 3,600 eV can able to interfere with Kα of Ca at 3,691 eV. However, the Sb can be identified in Kα at 26,360 eV. This can be seen if the detectors energy range is increased upto 30 times higher. In case of Pb in Kα at 74,969 eV, which is not possible to measure in the non-destructive method. This kind of complication might arise and lead to the false positive analysis due to matrices complexity of the inorganic element presence [4,8,10–13].

In case of destructive analysis, the difference between ICP-MS and ICP-OES is one detects with the mass and another detects with the atomic emission spectrum. Thereby, the mass spectrometry has high levels of accurate and precise in the isotopes, but the matrix effects causes the signal to interfere in the analysis. For example, the isotopes of Pb such as 206, 207 and 208 might able to interfere with each other based on polyatomic and isobaric interfering elements. In case of ICP-OES, each element will exhibit unique colour emission spectrum on the visible wavelength and leading to measure as total elemental analysis rather than isotopes. Most of the GSR might be in the form of solids present in the form of particulates in the substrate like cloth, wound and skin tissues, papers, leather, rubbers, etc. in those conditions, the substrate have to be digested properly to mineralize the elements to detect in ICP-OES. Few researchers reported in using nitric acid as digestion to extract the GSR in measuring ICP-OES. However, this process is more common as per environmental protection agency (EPA) acid digestion procedures [14–16].

Based on the above reported related to inorganic elements in the GSR, the measurement of inorganic GSR residues randomly, i.e selected elements such as Pb, Ba and Sb for understanding the distance fired were studied widely. Not all firearms will be using same type of compounds and materials in their ammunition. The database is scarce for the use of chemical compounds as well as the firearms. In such conditions, the analysis will be need to be understand based on the available evidence material like firearms, bullet, casing and bullet powder. Due to the complexity of the matrices types, inorganic chemical and firearms varieties, pin pointing the inorganic presence is there or not need to be studied along with the various fired distances. Few researchers have reported as distance increases the level of inorganic residues decreases [9,12,17,18]. Thereby, the present study will be using Indian small arms system (INSAS) rifle with single shot fired experiments in various distances from 0 to 300 cm are studied. Later, the substrates and gun powder (GP) will be processed with acid digestion method and measured in the ICP-OES used. Both the GP of INSAS firearms and analysis in ICP-OES is first time reporting to understand the inorganic GSR and GP relations either by matrix corrected and non-corrected statistical approach to pinpointing the possible inorganic elements involved in the substrate. Thereby, the direct analysis is possible during crime event in identifying the elements.

2. Experimental Section

2.1. Firing Setup

All the firing experimental setup was conducted in Police Training School, Karai, Gandhinagar, Gujarat, India. The substrate used in our study was filter paper (KALPI No 1) school grade rough routine quality fitted against the steel plate. The INSAS rifle with barrel length of 464 mm with ammunition size of 5.56 x 45 mm having gas operation with rotating bolt was fired as single shot. The firing distance were 0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 200 and 300 cm was carried out. The firing was carried out by the police personnel in their traditional way by point and shoot method. This was carried out to mimic the real-time environmental conditions. The samples such as fragmented and whole substrates were collected and kept in polyethylene sealed covers. The gun powder was collected from the non-fired bullet kept in polyethylene sealed bags. The sample was black in colour with macroscopic particles as shown in Figure 1 The total weight of the gun powder in a bullet was ~1.495 g. All the collected samples were transported to the Department of Forensic Medicine & Toxicology, Pramukhswami Medical College & Sri Krishana Hospital, Karamsad, Gujarat, India. Later shifted to Dr KC Patel Research and Development Centre, Charotar University of Science and Technology, Changa, Gujarat, India and stored in dark conditions for six months till the sample pre-treatment for measuring multi-elemental in spectroscopy instrument.

Figure 1: INSAS gun powder

2.2. Sample pre-treatment of GSR samples

Before the pre-treatment, all the GSR samples were photographed using mobile camera (Samsung A50 model, Samsung India Pvt. Ltd.). This helps us to identify the bullet holes, shrapnel, fragments or any bullet marks on the substrate. Later, the identified GSR samples in the substrate were used for acid digestions instead of whole substrates. The GSR samples were modified method of pre-treated with open vessel acid digestion procedure as per the environmental protection agency (EPA No 3050 B) was followed in our study. The substrate was weighed to ~0.5 g and spiking the ICP standard chromium of ~7 ppm in 100 mL borosilicate beaker as internal standards.

Further, the acids were added with 5 mL of concentrated nitric acid, 1 mL of concentrated hydrochloric acid, 1 mL of hydrofluoric acid and a few drops of hydrogen peroxide. Then, the samples were kept for 1-hour chemical equilibrium and later, initiated the digestion by heating the hot plate at 80oC and finally lead to evaporate to dryness. The digestion procedure was repeated for 3 times with above acids, overall the turnaround time for the process was 4 hours. Afterwards, the digested samples were re-dissolved into 5% nitric acid upto 15 mL and filtered the solvent in Whatman no 42. The filtrate was subjected to instrumental measurement for multi-elemental analysis [16,19].

2.3. Instrumental Parameters

The instrument used in our study was inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Pvt Ltd, USA). Table 1 shows the tuning parameter used in our study to measure the samples for multi-elemental analysis. The ICP based multi-elemental solution was used (Loba Chemie Pvt Ltd, India). There were 33 elements such as aluminium (Al), silver (Ag), arsenic (As), boron (B), barium (Ba), beryllium (Be), bismuth (Bi), calcium (Ca), cadmium (Cd), cesium (Cs), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), indium (In), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybedenum (Mo), sodium (Na), nickel (Ni), niobium (Nb), lead (Pb), rubidium (Rb), antimony (Sb), selenium (Se), strontium (Sr), titanium (Ti), thalium (Tl), vanadium (V), uranium (U) and zinc (Zn). All the standards both internal and multi-elemental standards were prepared in 5% nitric acid. The analytical limits of detection (LOD) and quantification was studied by acid digestion for our instrument as shown in supplementary Table 1. All the standards and samples were performed in n = 3 for repeatability and reproducibility measurement.

Table 1: ICP-OES tuning parameters

S.No	Parameter	Value
1	RF power	1350 W
2	Auxiliary gas flow	1.5 L/min
3	Coolant Gas flow	12 L/min
4	Nebulizer gas flow	0.35 L/min
5	Nebulizer gas pressure	0 kPa
5	Pump speed	50 rpm

2.4. Computation of measurement correction and statistical analysis

The measured data was further processed with correcting the data with internal standards correction as shown in equation (1). The corrected data was further analysed in statistical measurement such as Pearson, Spearman and Kendall correlation with principal component analysis (PCA) to identify the relation of elements in gun-shot residue on the substrate with distance based on the gun powder analysis. The statistical software was used in our study Origin Pro 2019 version.

$$C = \frac{M \times DF \times OD_B}{m \times R \times OD_S} \quad (1)$$

Where, the C is the concentration of samples (ng/g), M is the measured data of samples in ng/mL, DF is the dilution factor (mL), m is the mass of the sample used in digestion (g), R is the chemical recovery in the acid digested samples, ODB and ODS (ng/mL) is the obtained data from internal standard in blank and samples respectively.

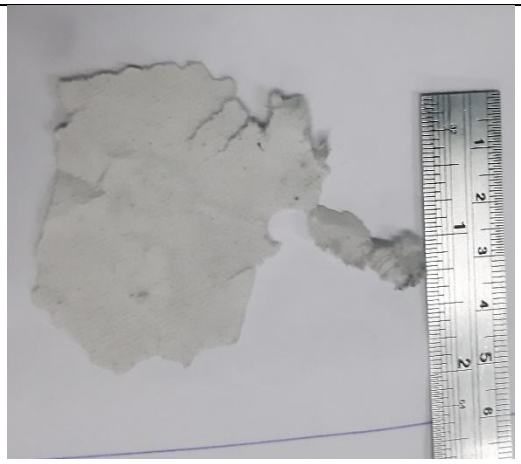
3. Results and Discussion

3.1. Photographic events of GSR samples

INSAS fired GSR samples were photographed as shown in the Figure 2. The photographic examinations were indicating the presence of bullet marks, sharpnels, fragments and black coloured residues on all substrates. This enables us to identify the GSR for further sample pre-treatment in measuring in ICP-OES. The close range contact between the firearms and substrate was made the substrate to be in pieces. However, the sharpnels, black colour and fragments were seen in the samples of 0 to 75 cm. Afterwards, marking of bullet holes entering were visible

in the substrates of 90 to 300 cm. As distance increases, the bullet holes remain averagely 1.22 ± 0.16 mm as shown in Table 2. This was observed in the measurement using the Image J software. The software computes only perimeter of the circle and thereby using equation (2) diameter of the circle was estimated. The hole diameter was similar to 9 mm bullet reported by researchers [9].

$$Diameter\ (cm) = \frac{perimeter}{\pi} \quad 2)$$



0 cm

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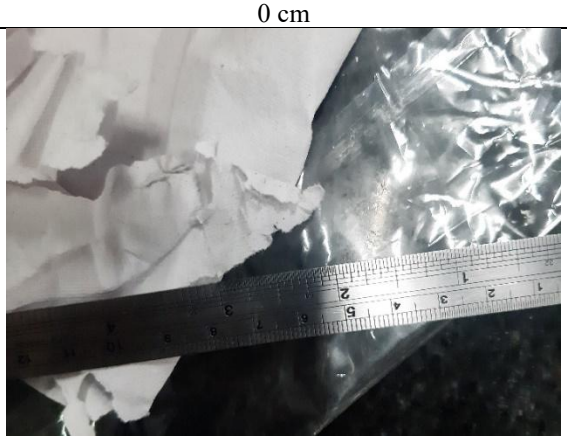

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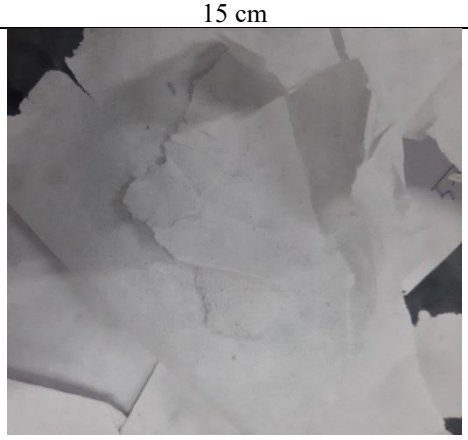
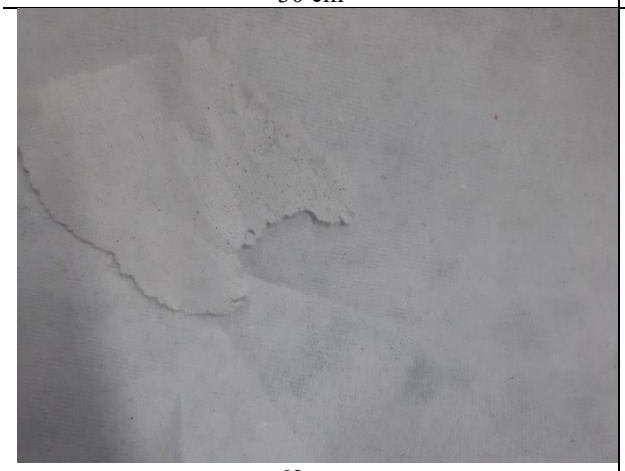
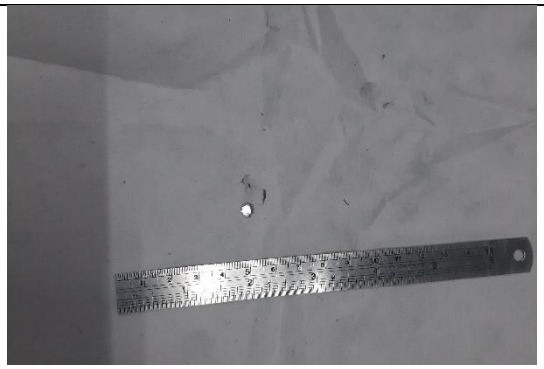


45 cm



60 cm

75 cm



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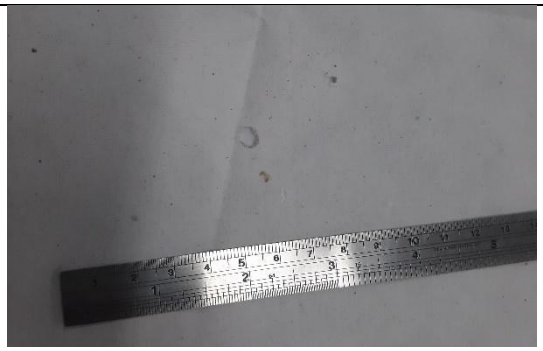
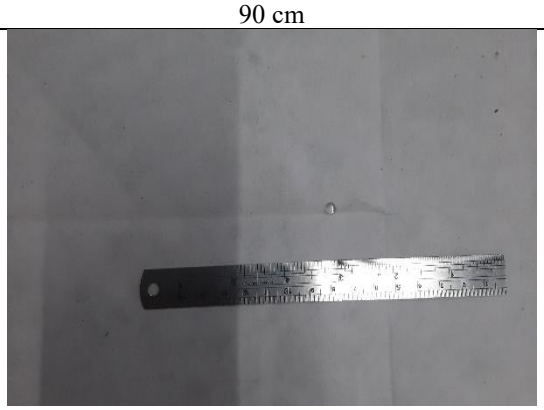
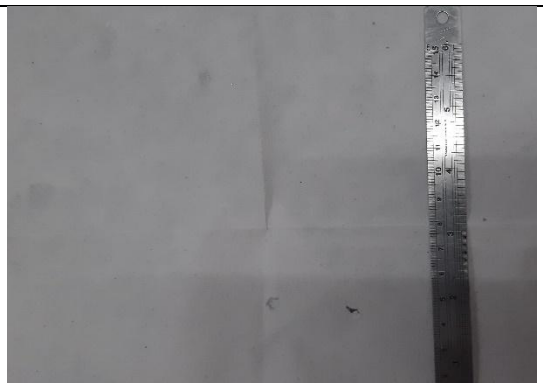


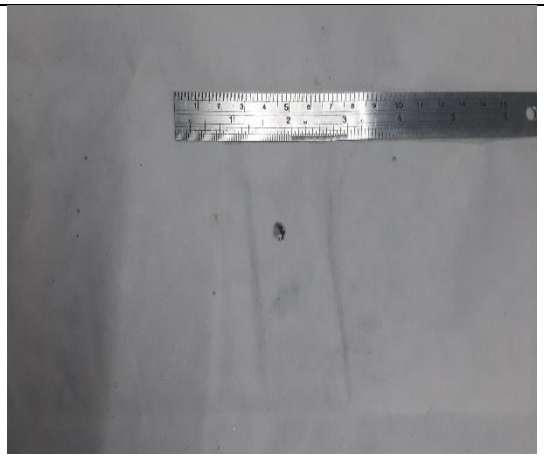
105 cm



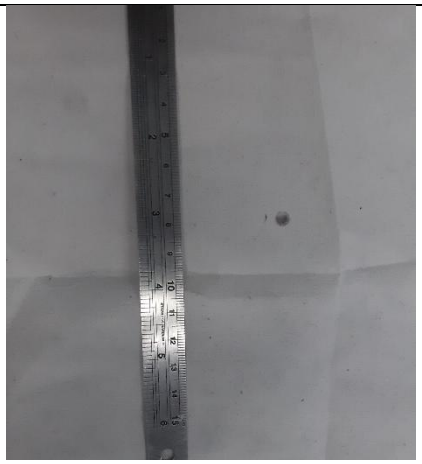
120 cm



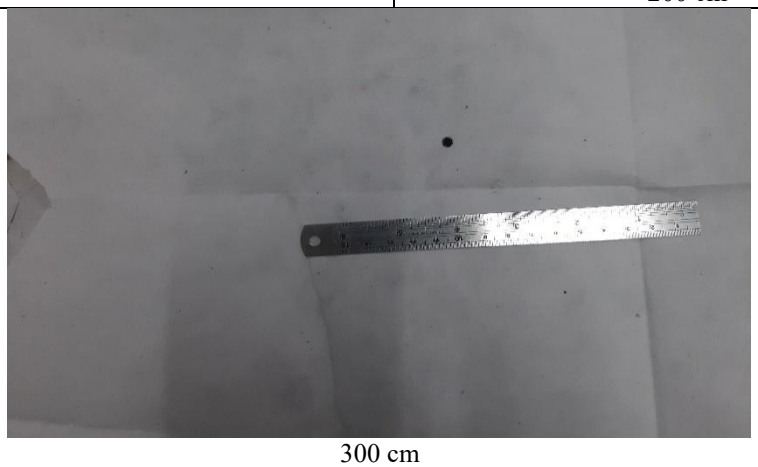
135 cm



150 cm



200 cm



300 cm

Figure 2: Photographic of bullet marks in various fired distance GSR samples

Table 2: Photographic measurement of bullet hole diameter of GSR samples

Distance (cm)	hole diameter (mm)
75	1.09
90	1.24
105	1.48
120	1.19
135	1.06
150	1.32
200	1.01
300	1.36

Similar studies were reported by various researchers in ammunition like 0.38 calibre in cotton (0, 5, 10, 50, 100 and 200 cm) [12], 9 mm in cloth (8, 15, 23, 30, 38 and 46 cm) [20], 7.62 mm in polyethylene terephthalate (PET) (0, 5, 10, 20, 50 and 100 cm) [21], and 9 mm in cotton cloth (5, 20, 40 , 80 and 100 cm) [8], 9 mm in cloth (5, 10, 25, 40, 50, 60 and 100 cm) [17], 7.65 in cotton cloth (25, 50, 75, 100 and 125 cm) [18]and 5.56 mm in cotton cloth (30 and 60 cm) [22]. Most of these studies do reported the bullet hole was observed and found >50 cm distance firing depending upon the bullet diameter. In our study, we found the bullet hole at 75 cm GSR samples and after 75 cm to 300 cm, the bullet hole was intact in the substrate. This shows that our study was first time reporting the more distances the hole remains visible and traces of GSR was present in the substrates. This was further analysed in ICP-OES for elemental mapping and concentration of elements present in the substrate.

3.2. Elemental Mapping in GSR samples and gun powder

The components present in INSAS fire arms gun powder and fired residues in the substrate were shown in supplementary Table 3. The elemental components were in the gun powder were in this higher concentration order Fe > U > Mg > Al > Ni > Zn > Mo > Mn > As > B > Sb > Sr > Li > Co > Cu > Ba > Pb > Ag > Cd. The samples collected from the substrate having the gun shot residue (GSR) fired at various distances. The mapping of elemental concentration of these GSR samples were shown in Table 3.

Table 3: Elemental Mapping of GSR in various distances shots fired in substrate

Distance	Elemental Mapping from higher to lower concentration order
0	Fe > Mg > Cu > Al > U > Ti > Pb > As > Zn > Sb > Ni > B > Sr > Ba > Mn > Mo > Co > Cd > Li > Ag.
15	Fe > Mg > Al > B > Ti > U > Cu > As > Pb > Zn > Sb > Ni > Sr > Ba > Mn > Mo > Li > Ag > Co > Cd.
30	Fe > Mg > Al > Cu > Ti > As > Pb > Ni > Zn > Sb > Sr > U > Ba > B > Mn > Mo > Co > Ag > Cd > Li.
45	Fe > Mg > Al > Cu > B > Ti > U > Pb > As > Zn > Sb > Ni > Ba > Sr > Mn > Li > Co > Cd > Ag.
60	Fe > Mg > Al > Cu > U > Ti > B > Pb > As > Zn > Ni > Sb > Ba > Sr > Mn > Mo > Li > Co > Ag > Cd.
75	Fe > Mg > Al > B > Ti > Cu > U > As > Pb > Ba > Zn > Sb > Ni > Sr > Mn > Mo > Li > Co > Cd > Ag.
90	Fe > Mg > Al > U > Ti > Cu > As > Ni > Zn > Sb > B > Sr > Ba > Pb > Mn > Mo > Li > Co > Ag > Cd.
105	Fe > Mg > Al > Ti > Cu > U > As > B > Ni > Zn > Sb > Sr > Pb > Ba > Mn > Mo > Li > Co > Cd > Ag.

120	Fe > Mg > Al > U > Ti > Cu > As > B > Ni > Zn > Sr > Sb > Ba > Mn > Mo > Li > Co > Pb > Cd > Ag.
135	Fe > Mg > Al > U > Ti > As > Cu > Ni > B > Zn > Sb > Sr > Ba > Mn > Pb > Mo > Li > Co > Ag > Cd.
150	Fe > Mg > Al > U > Ti > As > Cu > Ni > B > Zn > Sr > Sb > Mn > Ba > Li > Mo > Pb > Ag > Co > Cd.
200	Fe > Mg > B > Al > Ti > U > As > Cu > Ni > Zn > Sr > Sb > Mn > Ba > Mo > Co > Li > Ag > Cd > Pb.
300	Fe > Mg > Al > B > U > Ti > As > Cu > Ni > Zn > Sr > Sb > Mn > Ba > Li > Mo > Pb > Co > Cd > Ag.
Substrate	Fe > Mg > Al > U > Ti > As > Cu > B > Zn > Sr > Sb > Mn > Ba > Mo > Ni > Li > Pb > Co > Cd > Ag.

These concentrations were in higher ppm levels and due to the effect of substrate of filter paper. These major elements might be present in the filter paper. Thereby, blank of the substrate material was analysed as shown in Table 3 and supplementary Table 2. The elemental patterns of substrate were similar to the GSR samples. This was due to the matrix effect of elements exist in the substrate. However, compared to the gun powder, the concentration in the substrate was lower. This shows the mixture of these elements become insignificant to identify the elements reported in real crime applications. Hence, the matrix normalization will be an ideal approach to identify the probable elements as shown in supplementary Table 3. This was not possible with gun powder for matrix normalization. However, the matrix non corrected can be understand using the statistical analysis of correlation and covariance of the data. Based on the elements of matrix corrected data using MDQL, the GSR samples were shown in Table 4.

Table 4: Matrix corrected data based on MDQL

Distance	Elemental Mapping from higher to lower concentration order
0	Cu > Fe > Pb > Ni > Zn > Ba > Sr.
15	Fe > B > Cu > Ni > Zn > Ba > Sr > Mn.
30	Cu > Pb > Fe > Ni > Zn > Ba.
45	Cu > B > Pb > Fe > Ni > Zn > Ba > Ti.
60	Cu > Fe > Pb > B > Ni > Zn > Ba > Ti > Mn.
75	B > Cu > Fe > Ba > Zn.
90	Cu > Fe > Ni > Ba > Zn > Sr.
105	Fe > Cu > Ni > B > Ti > Zn > Ba > Sr > Mn.
120	Fe > Al > Cu > B > NI > Ti > Zn > Ba.
135	Fe > Ni > Ti > Ba > Zn.
150	Fe > Ni > Ti > Ba > Zn > Sr > Ba.
200	Fe > B > Ti > Ni > Sr > Zn > Ba > Mn.
300	B > Fe > Ni > U > Ti > Zn > Mn.

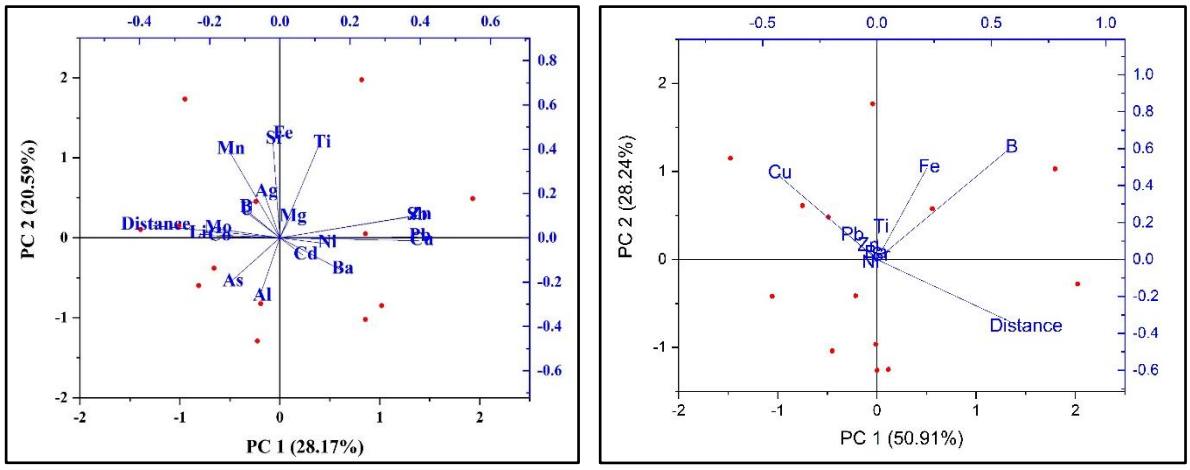
The MDQL was removed from this order to represent the elemental contents present in the GSR. The samples were predominant with Cu, Fe, Pb, Ni, Zn, Ba and Sr. Pb was able to exist from 0 to 60 cm. Similarly, Cu was

able to exist from the 0 to 120 cm. Only Fe, Ni, Zn, Ba is existing from 0 to 300 cm of the GSR. Other elements like B, Sr, Ti, Mn and Al were present in occasionally. These might be due to the external interferences in the samples. Based on these available data, both treated (matrix correction) and untreated (matrix non-corrected). The significance is very different; this can be proven with the statistical data by comparing both the data to understand the prominent elements present in the GSR samples based on the GP. Few researchers have reported for 5.62 mm bullet based on INSAS elemental analysis were Pb > Ti > Ca > Fe > Cu > Ba > Zn > S and absence of Sb. This is uncertain with XRF measurement due to the spectral overlap or cross interference were the chances in Lβ of Pb at 10,550 eV can able to interfere with Kα of As 10,543 eV based on the X-ray emissions and Lβ of Sb at 3,600 eV can able to interfere with Kα of Ca at 3,691 eV. The Sb can be identified in Kα at 26,360 eV and in case of Pb in Kα at 74,969 eV was not possible until the detectors energy range must be increased upto 30 – 100 keV. The present study showed the matrix non-corrected has the presence of As and Ca in the substrate. Therefore, the possibility of spectral overlap or cross interferences might occur in either XRF or SEM EDS. The more accurate and precise analysis for measuring inorganic element was ICP-MS, but the abundance of isotopic elements plays an important role for correcting the concentration data, which is not possible due to the metallurgy of the firearms, GP, cases, substrate and environmental mixture leading for polyatomic and isobaric interferences. Thereby, ICP-OES method using atomic emission of each element will be unique and various researchers were reported for measuring GSR [11,14,22].

In our study, the use of nitric acid along with hydrochloric and hydrofluoric acid played an important role for leaching the metals from the substrates. The chemical recovery via open digestion vessel were ranging from 89.5 to 112% from the 13 GSR samples. Each recovery and internal standard corrections were made as per the equation (1). This will not correct the matrix, but shows the concentration of metals present in the substrate. However, the present study was able to correct the matrices using the substrate (paper) and not in the case of bullet powder, where the purity of the chemicals were unknown. Identifying these metals in GSR will be difficult without matrices correction. This scenario will be occurring mostly in crime scene were matrix blank is required. Hence, the present study uses the statistical approach to understand the differences matrices corrected and non-corrected might be approachable method in the real-time samples i.e. GSR evidences in crime scenes.

3.3. Statistical Analysis of GSR with distances and probable inorganic elements

The present study was performed with two ways of statistical approach based on data 1) matrix non-corrected and 2) matrix corrected. The corrected means that the matrice blank was subtracted from the substrate without any firearms shots. Thereby, the relation will be specific towards the firearms and GP. There are two methods of statistical approached in the study for those data were correlation and covariance. The correlation study was approached with Spearman. In case of covariance, we carried out with principal component analysis (PCA). Figure 3 and supplementary Table 4 shows the PCA of matrice non-corrected and corrected data. The elements related to firearms and GP with relation to distance fired in all the substrates were observed the elements such as Cu, Pb, Ni, B, Ba, Fe, Sr, Ti and Zn. Using the covariance, the analysis clearly indicated no relation of GP with elements like Sb, Ag, Al, As, Cd, Co, Li, Mg, Mn, Mo and U. The angle between the distance of each elements having acute, obtuse and perpendicular angle relation showing positive, negative and no correlation. The Cu with distance were showing 173.31º (non-corrected) and 163.41º (corrected). Similarly, the Pb relation with distance were observed the angle of 170.76º (non-corrected) and 163.65º (corrected). This shows the non-corrected data was higher degree than the corrected data due to the proper matrices substrate correction applied in the analysis. However, the angular distance for Ba and Zn were following opposite direction like 148.85º (non-corrected) and 151.12º (corrected) and 156.74º (non-corrected) and 156.1º (corrected) respectively. Similar patterns were observed in Fe, B, Sr and Ti. These elements have no relation with distance based on GP traces on the substrates. But can be used as qualitative signature pattern along with Cu and Pb, where these two elements were decreasing concentration with increasing distances.



a) b)

Figure 3: PCA biplot for GSR mapping with distance on matrices a) non-corrected data and b) corrected data

This was further confirmed with Spearman correlation analysis of both the datas as shown in supplementary Table 5. The non-corrected and corrected data shows the highly significant at 0.05 level for the elements such as Cu, Pb, Ba and Zn with 92-93%, 81-89%, 65% and 91% respectively. The presence of Cu and Pb might come either from bullet jacket or GP as lead styphante. This was widely reported by many researchers as pre-dominant signature in firearms depots. The environmental levels of Pb were in the range from 13% to 300% in soil, 0.18 to 2.5 mg/L in water and 54 to 133 ng/mL in shooters blood. Similarly, Cu levels were in the range from 1.08% to 5.2% in soil, 0.63 to 1.6 mg/L in water and 10 to 37 ng/mL in breathing zone [23–27]. This shows the regardless of the Sr, Zn, Ni, and Ti, the Cu and Pb ratios will be important signature for shooting from INSAS firearms with 5.56 mm bullet. Apart from, the rest of the elemental was not possible to detect due to MDQL. Similar trend might be possible for other ammunition to estimate the distance fired from the firearms. This study reveals that the INSAS rifle signature elements were Cu and Pb with distance fired.

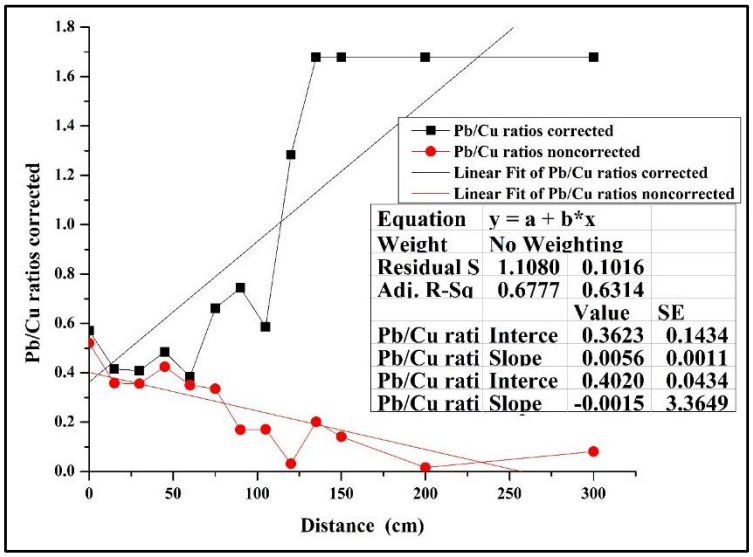


Figure 4: Pb to Cu ratio regression with 5.56 mm ammunition (graph is tentative)

Table 5: Comparison between the reported literature for various firearms

S.No.	Type of ammunition	Elemental Mapping	Type of analytical detection	Maximum Distance Reported for GSR	Concentration range of GSR	References
1.	0.38 calibre	Pb, Ba, Sb	Colorimetric and digestion with ICP-OES	0, 5, 10, 50, 100 and 200 cm	8.3 to 3158 ng/mL	[12]
2.	9 mm with different bullet metal composition (CuZn10, CuZn30, CuZn30 with Pb:Sb core)	Pb, Sn, Cu, Zn	ICP-OES	5, 20, 40 cm	4 to 3000 ng/mL	[8]
3	9 mm	Pb	Microfluidic paper device using sodium rhodizonate reagent	5, 10, 25, 40, 50 and 60 cm	100 to 400 mg/mL	[17]
4	9 mm and 0.38 revolver	Ba, Pb, Fe	ICP-MS using organic extraction	Not reported	3 to 9 ng	[28]
5	7.65 mm	Pb, Sb, Ba	SEM EDS	50 to 100 cm	37 to 657 particles	[18]
6.	9 mm	Pb, Sb, Ba	SEM EDS	10, 20, 30, 50, 70, 100 cm	70 to 190 particles	[5]
7	0.4 calibre	Pb, Ba, Sb, Al, Ti, Cr, Mo, Cu, Zn and Sr	ICP-MS with acid digestion	Shooters Hand	2.64 ng/mL	[29]
8	7.62 mm	Pb, Ba, Sb, Ti, and Zn for toxic and non-toxic primers	ICP-MS with acid digestion	Not reported	6.5 to 854 ng/mL	[15]
9.	9 mm	K, Ti, Cu, Zn, Sb, Ba, Pb and Bi in lead free and leaded ammunition	ICP-MS with acid digestion	Not reported	0.012 to 11 µg/mL	[13]
10.	9 mm	S, Ca, K, P, Fe, Mn, Cu, Zn, Ho, Cs, Ag, Sb, Hg, Si, Ni, Br, Pb, Ti, Th, C, O, Al, Cr, Sb, Ba	SEM EDS	0, 30, 100, 150, 400 and 500 cm	0.01 to 96%	[9]

11	5.56 mm	S, Ca, Ti, Fe, Cr, Zn, Ba, Sb, Pb, K	Micro-XRF	12 inch and 24 inch	9.6% to 107%	[22]
12	5.56 mm with INSAS	Cu and Pb based on PCA and correlation statistical approach	ICP-OES with acid digestion	0, 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, 200 and 300cm	36.64 to 227.74 µg/mL	Our study

The Pb to Cu ratios were able to predict upto 90 cm for non-corrected data and for corrected data, prediction was possible to 105 cm as shown in Figure 4. The otherway around Cu to Pb ratios will lead to > 1.5 ratios in the distance measuring. Apart from this, the transfer of Pb to Cu in the samples will be identifiable by various researchers as shown in Table 5 of 9mm and 0.4 calibre. This was first time reporting the Pb to Cu ratios in the distance based measurement as approximate as shown in Figure 4. However, this approximately estimating the shooters distance based for corrected data was 67% and non-corrected data of 63% based on linear regression model of the data. The study reveals for 5.56 mm with INSAS firearms, the distance estimate was qualitative not as quantitative. This was possible till 150 cm for corrected data and 100 cm for non-corrected data. Similar studies with other instruments like SEM EDS and XRF might make difficult to detect the trace metallic elements due to the spectral interferences. Thereby, such studies have to be conducted for other firearms with various bullet casing and GP in ICP-OES for database development. This study also shows that the GP of this ammunition was not correlating with the GSR on the substrates due to the chemical migration factor mechanism of explosive in the barrel and bullet casing will be different. Hence, alternative techniques like colorimetric for Cu and Pb need to be developed to detect in the range of 10 to 20 ng/mL for far distance GSR mapping in rapid analysis in crime scene based on our study.

4. Conclusion

The present study reports the 5.56 mm ammunition from INSAS firearms shots in the substrate were identifiable using inorganic GSR. The bullet hole was visible in the substrate at 75 cm and hole intact in the substrate was found in 75 to 300 cm via photography. The average hole diameter in substrate was 1.22 ± 0.16 mm. This was similar to other ammunitions like 9, 7.62,7.65, 5.65 mm and 0.34 calibre. Based on the bullet hole size, the type of ammunition will be difficult due to the near similar size of other types of ammunitions were available. However, using chemical signature of the ammunitions the type of bullet ammunitions material will be able to determine. The study found the GP without matrice corrected have the elemental map in this order: Fe > U > Mg > Al > Ni > Zn > Mo > Mn > As > B > Sb > Sr > Li > Co > Cu > Ba > Pb > Ag > Cd. However, the GSR from the substrates were not able to relate with GP due to environmental contaminations were possible. Using matrice corrected, the elemental signature was able to determine with distance. The Pb was able to exist from 0 to 60 cm in the substrates. For Cu was from 0 to 120 cm and Fe, Ni, Zn, Ba is present from 0 to 300 cm of the GSR. There were other elements like B, Sr, Ti, Mn and Al present in occasionally and not following trend. This was further compared with the statiscal approach of Spearman correlation and PCA (co-variance). Among them Cu and Pb were the possible elements from 5.65 from INSAS firearms upto 92-93% and 81-89% respectively for both matrice corrected and non-corrected data. This was lead us to possible approximation on firearm distance. Matrice correction was possible from evidence samples. This has to be comply by collecting the substrate away from the GSR sites in crime scene and might be an additional evidence to recreate in crime scene. Using XRF and SEM EDS will able to help the qualitative analysis rather than quantitative as cross interference might occur in the X-ray emission detection. Thereby, quantifying the elemental mapping via ICP-OES was better analytical choice. The firing distance using Pb to Cu ratios was able to estimate the firing distances upto 60 cm and maximum it can indicate upto 105 cm distances to correlate with the ammunitions and firearms with the help of statistical approaches. Based on the current study, the development of alternative techniques like colorimetric need to be developed using specific IGSR elements at lower concentration ranging till 10 to 20 ng/mL.

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6. Conflict of Interest

The authors declare no conflict of interest

7. Supplementary Tables

Supplementary Table 1: Analytical limits of ICP OES analysis using acid digestion method

Element Name	Slope	Standard Error	Adj. R-Square	All the units were ng/mL			
				Detection Limit	Limit of Detection (3 sigma)	Limit of Quantification (10 sigma)	Method Detection Quantification Limit (MDQL)
Ag	0.99976	0.00533	0.9998	35	105	350	12
Al	1.00197	0.00387	0.9999	137	410	1367	46
As	0.99863	0.00196	0.99997	95	285	951	32
B	0.99928	0.00223	0.99997	50	150	500	17
Ba	1.00004	0.01315	0.99879	3	9	30	1
Cd	0.99987	0.00469	0.99985	9	27	90	3
Co	0.99961	0.00534	0.9998	27	81	270	9
Cr	0.99928	0.00575	0.99977	50	150	500	17
Cu	1.00121	0.00487	0.99983	84	252	839	28
Fe	0.99935	0.00452	0.99986	45	135	450	15
Li	1.00089	0.02419	0.99592	62	186	619	21
Mg	0.99947	0.00445	0.99986	37	111	370	12
Mn	0.99994	0.00753	0.9996	4	12	40	1
Mo	1.00032	0.00344	0.99992	22	66	220	7
Ni	0.99983	0.00308	0.99993	12	36	120	4
Pb	1.00204	0.00443	0.99986	141	422	1407	47
Sb	1.00227	0.00342	0.99992	157	470	1566	52
Sr	0.99996	0.00865	0.99948	3	9	30	1
Ti	1.00022	0.00569	0.99977	15	45	150	5
U	0.99949	0.01388	0.99865	35	105	350	12
Zn	1	0.00497	0.99983	3	9	30	1
Pre-concentration Factor - 30							

Supplementary Table 2: Multi-elemental concentrations in various distances shot fired from INSAS 5.62 mm bullet

Distance (cm)	Fe	Mg	Al	Ti	U	Cu	B	As	Pb	Ni	Zn	Sb	Sr	Ba	Mn	Mo	Li	Co	Ag	Cd
0	764 ± 51	450 ± 30	249± 16	155 ± 12	162 ± 19	257 ± 18	29 ± 1	59 ± 3	134 ± 9	38 ± 2	46 ± 3	41 ± 2	19 ± 2	14 ± 2	10 ± 1	6 ± 0.4	2 ± 0.3	2 ± 0.1	1 ± 0.1	2 ± 0.1
15	826 ± 56	510 ± 34	206 ± 13	178 ± 13	155 ± 18	148 ± 10	179 ± 9	55 ± 2	53 ± 4	32 ± 2	39 ± 3	35 ± 2	23 ± 2	18 ± 2	11 ± 1	6 ± 0.4	4 ± 1	2 ± 0.1	3 ± 0.2	2 ± 0.1
30	649 ± 44	386 ± 26	219 ± 14	112 ± 8	13 ± 2	156 ± 11	13 ± 1	58 ± 3	56 ± 4	41 ± 2	34 ± 2	27 ± 2	16 ± 2	13 ± 2	10 ± 1	6 ± 0.3	2 ± 0.2	3 ± 0.2	2 ± 0.1	2 ± 0.1
45	661 ± 44	422 ± 28	327 ± 20	120 ± 9	77 ± 9	175 ± 12	146 ± 7	56 ± 3	74 ± 5	28 ± 2	34 ± 2	31 ± 2	17 ± 2	19 ± 2	9 ± 1	6 ± 0.3	2 ± 0.3	1 ± 0.1	1 ± 0.1	1 ± 0.1
60	722 ± 49	508 ± 34	422 ± 26	120 ± 9	165± 20	217 ± 15	90 ± 4	42 ± 2	76 ± 5	38 ± 2	40 ± 3	36 ± 2	17 ± 2	26 ± 3	11 ± 1	8 ± 1	5 ± 1	3 ± 0.2	1 ± 0.1	1 ± 0.05
75	630 ± 42	446 ± 30	427 ± 27	116 ± 9	93 ± 11	100 ± 7	266 ± 13	80 ± 4	34 ± 2	20 ± 1	28 ± 2	25 ± 2	17 ± 2	29 ± 3	10 ± 1	7 ± 0.4	6 ± 1	3 ± 0.2	2 ± 0.2	2 ± 0.2
90	652 ± 44	557 ± 37	344 ± 21	98 ± 7	153 ± 18	92 ± 6	21 ± 1	66 ± 3	16 ± 1	43 ± 2	26 ± 2	21 ± 1	18 ± 2	17 ± 2	10 ± 1	8 ± 1	3 ± 0.4	2 ± 0.1	1 ± 0.1	1.2 ± 0.1
105	729 ± 49	417 ± 28	248 ± 15	141 ± 11	71 ± 8	109 ± 8	54 ± 3	57 ± 3	19 ± 1	37 ± 2	30 ± 2	28 ± 2	19 ± 2	17 ± 2	12 ± 1	8 ± 1	7 ± 1	3 ± 0.2	1 ± 0.1	2 ± 0.1
120	690 ± 46	502 ± 34	454 ± 28	120 ± 9	161 ± 19	66 ± 5	58 ± 3	65 ± 3	2 ± 0.1	36 ± 2	25 ± 2	15 ± 1	17 ± 2	12 ± 1	11 ± 1	8 ± 0.4	4 ± 1	3 ± 0.2	1 ± 0.1	1 ± 0.1
135	6801 ± 46	407 ± 27	282± 18	119 ± 9	148 ± 17	43 ± 3	37 ± 2	58 ± 3	9 ± 1	40 ± 2	23 ± 2	21 ± 1	17 ± 2	13 ± 2	11 ± 1	7 ± 0.4	4 ± 1	3 ± 0.2	2 ± 0.1	1 ± 0.1
150	693 ± 47	408 ± 27	192 ± 12	121 ± 9	138 ± 16	36 ± 3	25 ± 1	62 ± 3	5 ± 0.3	29 ± 2	21 ± 2	16 ± 1	18 ± 2	10 ± 1	11 ± 1	6 ± 0.4	8 ± 1	2 ± 0.2	3 ± 0.2	1 ± 0.1
200	848 ± 57	466 ± 31	217 ± 14	152 ± 12	92 ± 11	32 ± 2	253 ± 12	59 ± 3	1 ± 0.03	30 ± 2	26 ± 2	20 ± 1	23 ± 2	10 ± 1	12 ± 1	8 ± 0.4	3 ± 0.4	3 ± 0.2	2 ± 0.2	1 ± 0.1
300	747 ± 50	431 ± 29	366 ± 2	123 ± 9	215 ± 25	33 ± 2	224 ± 11	59 ± 3	3 ± 0.2	25 ± 1	21 ± 2	15 ± 1	17 ± 2	8 ± 1	11 ± 1	7 ± 0.4	7± 1	2 ± 0.1	1 ± 0.04	1.3 ± 0.1
5.62 mm GP	1085 ± 73	320 ± 21	186 ± 12	0.1 ± 0.01	334 ± 39	9 ± 1	16 ± 1	17 ± 1	4 ± 0.3	145 ± 8	38 ± 3	16 ± 1	14 ± 1	6 ± 1	21 ± 2	32 ± 2	11 ± 2	11 ± 1	2 ± 0.2	1 ± 0.04
Subst	605.38 ±	560.58 ±	402.0	111.4	199.58 ±	28.87 ±	23.92 ±	63.30	3.55 ±	4.97 ±	18.95 ±	14.98 ±	16.4 ±	7.85 ± 0.9	9.89 ±	6.07 ±	4.06 ±	2.1 ±	1.3 ± 0.1	1.39 ± 0.1

rate	40.68	37.39	1 ± 25	1 ± 8.4	23.51	2.01	1.13	± 2.8	0.24	0.28	1.34	0.98	1.53		0.86	0.36	0.63	0.15		

Supplementary Table 3: Normalized elemental concentration in GSR

Distance cm	Fe	Mg	Al	Ti	U	Cu	B	As	Pb	Ni	Zn	Sb	Sr	Ba	Mn	Mo	Li	Co	Ag	Cd
0	**158.6 ± 10.7**	≤ MDQL	≤ MDQL	43.4 ± 3.3	≤ MDQL	**227.7 ± 15.9**	≤ MDQL	≤ MDQL	129.9 ± 8.6	**32.5 ± 1.8**	**27.4 ± 1.9**	≤ MDQL	2.3 ± 0.2	**6.4 ± 0.7**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
15	**220.9 ± 14.8**	≤ MDQL	≤ MDQL	66.5 ± 5.0	≤ MDQL	**118.7 ± 8.3**	155.4 ± 7.3	≤ MDQL	49.2 ± 3.2	**27.2 ± 1.5**	**20 ± 1.4**	≤ MDQL	6.5 ± 0.6	**9.7 ± 1.1**	1.5 ± 0.1	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
30	**43.6 ± 2.9**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	**127.4 ± 8.9**	≤ MDQL	≤ MDQL	52.1 ± 3.4	**35.9 ± 2**	**15.3 ± 1.08**	≤ MDQL	≤ MDQL	**4.9 ± 0.5**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
45	**55.7 ± 3.7**	≤ MDQL	≤ MDQL	8.4 ± 0.6	≤ MDQL	**145.7 ± 10.2**	122.1 ± 5.7	≤ MDQL	70.6 ± 4.7	**23.09 ± 1.2**	**15.03 ± 1.06**	≤ MDQL	≤ MDQL	**11.1 ± 1.2**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
60	**116.2 ± 7.8**	≤ MDQL	≤ MDQL	8.3 ± 0.6	≤ MDQL	**188.3 ± 13.1**	66.1 ± 3.1	≤ MDQL	72.4 ± 4.8	**33.3 ± 1.8**	**21.15 ± 1.49**	≤ MDQL	≤ MDQL	**18.3 ± 2.1**	1.2 ± 0.1	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
75	**24.9 ± 1.7**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	**71.08 ± 5.0**	242.1 ± 11.4	≤ MDQL	≤ MDQL	**14.8** 0.8	**8.73 ± 0.62**	≤ MDQL	≤ MDQL	**21.5 ± 2.4**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
90	**46.1 ± 3.1**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	**63.1 ± 4.4**	≤ MDQL	≤ MDQL	≤ MDQL	**37.9 ± 2.1**	**7.31 ± 0.52**	≤ MDQL	1.7 ± 0.1	**9.3 ± 1.08**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
105	**123.4 ± 8.3**	≤ MDQL	≤ MDQL	29.08 ± 2.2	≤ MDQL	**80.2 ± 5.6**	29.5 ± 1.3	≤ MDQL	≤ MDQL	**32.07 ± 1.7**	**10.58 ± 0.75**	≤ MDQL	3.03 ± 0.2	**9.1 ± 1.05**	1.67 ± **0.15**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
120	**84.8 ± 5.7**	≤ MD	51.8± 3.2	8.8 ± 0.7	≤ MD	**36.6 ± 2.6**	33.7 ± 1.5	≤ MD	≤ MD	**31.4 ± 1.7**	**5.60 ± 0.40**	≤ MD	≤ MD	**3.6 ± 0.4**	≤ MD	≤ MD	≤ MD	≤ MD	≤ MD	≤ MD

		QL			QL			QL	QL			QL	QL		QL	QL	QL	QL	QL	QL
135	**75.3 ± 5.1**	≤ MDQL	≤ MDQL	7.8 ± 0.6	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	**35.2 ± 1.9**	**3.76 ± 0.26**	≤ MDQL	≤ MDQL	**5.1 ± 0.5**	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
150	**87.2 ± 5.9**	≤ MDQL	≤ MDQL	9.9 ± 0.8	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	**23.6 ± 1.3**	**2.27± 0.16**	≤ MDQL	1.8 ± **0.1**	**2.3 ± 0.2**	1.13 ± 0.10	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
200	**242.3 ± 16.3**	≤ MDQL	≤ MDQL	40.8 ± 3.1	≤ MDQL	≤ MDQL	228.7 ± 10.7	≤ MDQL	≤ MDQL	**24.6 ± 1.3**	**6.56± 0.46**	≤ MDQL	6.9 ± 0.6	**2.3 ± 0.2**	1.70 ± 0.15	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
300	**141.3 ± 9.5**	≤ MDQL	≤ MDQL	11.54 ± 0.9	14.9 ± 1.7	≤ MDQL	199.9 ± 9.4	≤ MDQL	≤ MDQL	**19.8 ± 1.1**	**2.03 ± 0.14**	≤ MDQL	≤ MDQL	≤ MDQL	1.32 ± 0.12	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL	≤ MDQL
MDQL	15	12	46	5	12	28	17	32	47	4	1	52	1	1	1	7	21	9	12	3

Supplementary Table 4: Extracted eigen vectors of PCA

Parameter	Matrices non-corrected			Matrices corrected		
	Coefficients of PC 1	Coefficients of PC 2	Angle of Vector of PCA	Coefficients of PC 1	Coefficients of PC 2	Angle of Vector of PCA
Distance	-0.36131	0.05533		0.64051	-0.37044	
Cu	0.39704	-0.01395	173.31º	-0.43505	0.46058	163.41º
Pb	0.39206	0.00364	170.76º	-0.118	0.12389	163.65º
Sb	0.38409	0.0979	156.99º			
Ni	0.1278	-0.02591	177.25º	-0.03895	-0.02622	116.01º
Ag	-0.04611	0.20627	68.69º			
Al	-0.05766	-0.26528	86.44º			
As	-0.14109	-0.19993	63.49º			
B	-0.10356	0.13481	46.76º	0.57894	0.59916	76.02º
Ba	0.17182	-0.14343	148.85º	-0.01639	0.02719	151.12º
Cd	0.06613	-0.07923	138.56º			
Co	-0.17945	0.00669	6.57º			
Fe	0.00164	0.46617	81.49º	0.21715	0.4919	96.22º
Li	-0.24128	0.01701	4.67º			
Mg	0.02998	0.09262	99.23º			
Mn	-0.14655	0.39715	61.03º			
Mo	-0.18327	0.04085	3.85º			
Sr	-0.0203	0.44306	78.67º	0.00573	0.0147	98.74º
Ti	0.11354	0.42587	96.22º	0.00692	0.16798	117.68º
U	-0.10101	0.12194	41.65º			
Zn	0.3929	0.10197	156.74º	-0.04865	0.06681	156.1º

Supplementary Table 5: Spearman correlation

Matrices non-corrected data																				
	"Distance"	"Ag"	"Al"	"As"	"B"	"Ba"	"Cd"	"Co"	"Cu"	"Fe"	"Li"	"Mg"	"Mn"	"Mo"	"Ni"	"Pb"	"Sb"	"Sr"	"Ti"	"U"	"Zn"
Distance Corr.	1	-0.03297	0.06044	0.37912	0.21428	-0.65385*	-0.40659	0.47802	-0.92308*	0.14285	0.57692*	-0.18132	0.46703	0.43956	-0.2967	-0.89560*	-0.85714*	0.16483	0.00549	0.06593	-0.91758*
p-value	--	0.91485	0.84502	0.20140	0.48205	0.01534	0.16797	0.09849	6.85E-06	0.64151	0.03893	0.55329	0.10760	0.13286	0.32492	3.48E-05	1.81E-04	0.59047	0.98577	0.83054	9.91E-06
Matrices corrected data																					
	"Distance"				"B"	"Ba"			"Cu"	"Fe"					"Ni"	"Pb"		"Sr"	"Ti"		"Zn"
Distance Corr..	1				0.17521	-0.65385*			-0.91374*	0.14286					-0.2967	-0.81441*		-0.02389	0.01105		-0.91758*
p-value	--				0.56696	0.01535			1.2633E-5	0.64152					0.32492	6.9966E-4		0.93825	0.97142		9.9062E-6

Note: 2 -tailed test of significance is used, *: Correlation is significant at the 0.05 level

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