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Title: An exploratory study of the potential of LIBS for visualizing gunshot residue patterns

Authors: María López-López, César Alvarez-Llamas, Jorge Pisonero, Carmen García-Ruiz, Nerea Bordel

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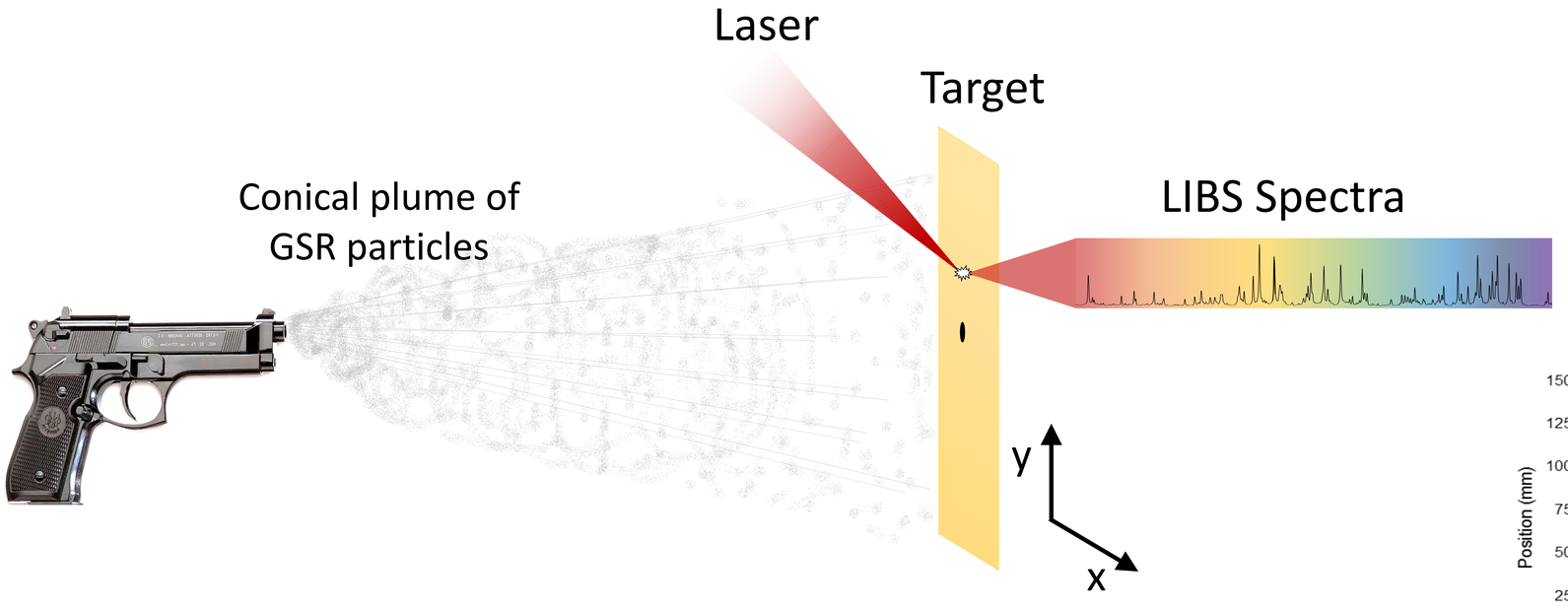
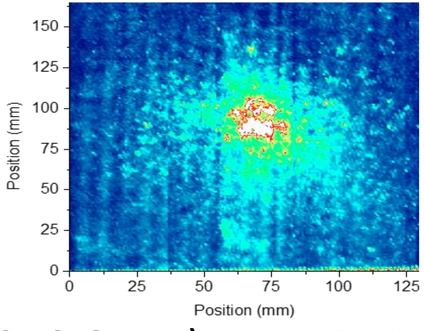
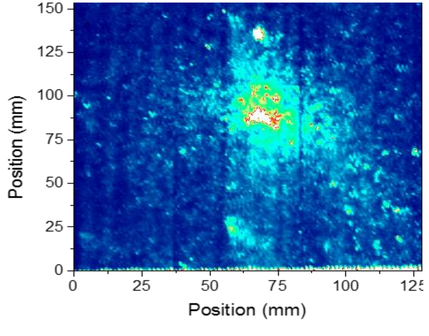



## GSR patterns

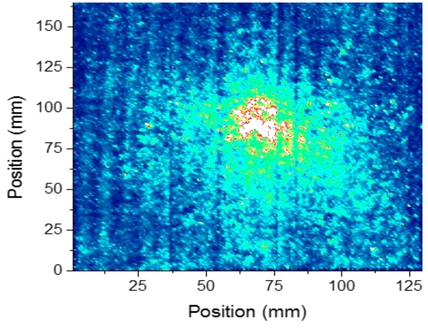
Pb I (283.3 nm)




Sb I (259.8 nm)




Ba II (455.4 nm)



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# An exploratory study of the potential of LIBS for visualizing gunshot residue patterns

María López-López [a, *], César Alvarez-Llamas[b, *], Jorge Pisonero [b], Carmen García-Ruiz [a], Nerea Bordel [b, □]

[a] Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering & Research Institute of Police Sciences, Edificio Polivalente de Química, University of Alcalá, Ctra. Madrid-Barcelona Km. 33.600, 28871 Alcalá de Henares (Madrid) Spain.

[b] University of Oviedo, Faculty of Science, Department of Physics, c/ Calvo Sotelo s/n, 33006 Oviedo, Spain.

□ Corresponding author: Nerea Bordel, Phone: +34 985103427, e-mail: bordel@uniovi.es

* Both authors contributed equally to this work

**Keywords**

LIBS, gunshot residues, distance estimation, forensic analysis, imaging

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**Highlights**

- The capabilities to perform GSR elemental analysis by LIBS has been proved.
- The GSR elemental distribution pattern has been highlighted using LIBS.
- The capability to perform a LIBS reanalysis of the sample has been demonstrated.

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# An exploratory study of the potential of LIBS for visualizing gunshot residue patterns

**Abstract**

The study of gunshot residue (GSR) patterns can assist in the reconstruction of shooting incidences. Currently, there is a real need of methods capable of furnishing simultaneous elemental analysis with higher specificity for the GSR pattern visualization. Laser-Induced Breakdown Spectroscopy (LIBS) provides a multi-elemental analysis of the sample, requiring very small amounts of material and no sample preparation. Due to these advantages, this study aims at exploring the potential of LIBS imaging for the visualization of GSR patterns. After the spectral characterization of individual GSR particles, the distribution of Pb, Sb and Ba over clothing targets, shot from different distances, were measured in laser raster mode. In particular, an array of spots evenly spaced at 800 µm, using a stage displacement velocity of 4 mm/s and a laser frequency of 5 Hz was employed (e. g. an area of 130 × 165 $mm^2$ was measured in less than 3 hours). A LIBS set-up based on the simultaneous use of two spectrographs with ICCD cameras and a motorized stage was used. This set-up allows obtaining information from two different wavelength regions (258-289 and 446-463 nm) from the same laser induced plasma, enabling the simultaneous detection of the three characteristic elements (Pb, Sb, and Ba) of GSR particles from conventional ammunitions. The ability to visualize the 2D distribution GSR pattern by LIBS may have an important application in the forensic field, especially for the ballistics area.

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## 1. Introduction

Gunshot residues (GSR), also known as cartridge discharge residues or firearms discharge residues, are particles produced during the discharge of a firearm [1]. These particles, typically of micron dimensions, are a mixture of organic compounds, coming mainly from the propellant, and inorganic compounds from the primer, propellant, cartridge case, bullet or the firearm itself. GSR particles are launched with the projectile and are transferred to the victim (target), the shooter or to different objects at the scene. In addition, after leaving the firearm bore, the GSR particles result in a conical plume of particles that creates a pattern on the target depending on different factors. The factors that affect the appearance of these GSR patterns include the type of ammunition and firearm, barrel length, firing angle, atmospheric conditions, target material, muzzle-to-target angle and, especially the firing distance [2]. Thus, a question commonly asked to the forensic firearm analysts, besides the identification of the GSR particles, is the estimation of the shooting distance (muzzle to target distance). This range, which has an extensive forensic significance for the reconstruction of a firearm-related offense, is estimated by the examination of the bullet entry hole and its surroundings [3].

Tests based on color chemical reactions that reveal the presence of nitro groups or heavy metals (e.g., Walker test, Marshal and Tewari test, sodium rhodizonate test, etc.) are used by the forensic analysts to visualize the GSR particles in the patterns. [1]. Color tests show important drawbacks like non-specificity to GSR, application using long and tedious proceedings, requirement of proper storage and disposal of the hazardous chemicals. Therefore, some other interesting approaches for shooting distance estimation not based on color chemical tests were reported in the literature. A recent review covers the latest methods proposed in this new field [3]. Visual methods based on video spectral comparators [4], digital infrared imaging [5], or light microscopy and image analysis [6,7], as well as instrumental approaches for elemental analysis, like X-ray Fluorescence [8], Atomic Absorption Spectroscopy [9], or Inductively Coupled Plasma Mass Spectrometry [10] were proposed to visualize GSR patterns. The main advantage of elemental techniques is the capability to perform simultaneous multielemental analysis, which provides valuable information.

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Laser Induced Breakdown Spectroscopy (LIBS) is an analytical technique that allows performing simultaneous multielemental analysis. LIBS is based on the use of a short duration laser pulse (on the order of ns or below) focused on a small area of the sample. The high fluence (energy per area) over the sample surface produces the ablation of a tiny quantity of sample and the formation of a laser-induced plasma. The species present in the plasma suffer processes of atomization, ionization and excitation; and the radiation coming from the excited species can be detected by an spectroscopic device [11]. LIBS provides some advantages over other methods of elemental analysis, such as simple and rapid analysis, or the requirement of very small amounts of material (~ 0.1 μg). Moreover, it has the possibility for stand-off and in-lab capabilities of analysis, and little or no sample preparation is required [12,13]. In view of these benefits, some works reported the use of LIBS for the identification of GSR particles.

Dockery and Goode [14] used LIBS to determine whether the hands of a suspected gun user contained traces of GSR. The GSR particles were collected by dabbing with adhesive tape the hands of shooters as well as volunteers that have not fired a gun within 24 h before sampling (only one type of firearm and ammunition was employed). Positive results were obtained in case of samples collected from the hands of a shooter, who fired multiple shots, or in the case that the gun was not cleaned before the shot. However, this positive identification is actually not so simple in case of a single shot using a clean gun. In a second work [15], the same research group investigated the period of time that a shooter will test positive for GSR after firing six shots with a revolver and afterwards continuing normal daily activities. Samples were collected at multiple hour intervals using the same collection approach above mentioned. The Ba II emission line at 455.403 nm was used as evidence of GSR presence. The authors claimed that, statistically, the results were positive for GSR 5.27 days after a firearm discharge.

A similar, but broad investigation, was performed some years later by Silva et al [16]. Different types of ammunition cartridges were fired using two different firearms. The hands of the shooters were sampled just after firing, and also after washing their hands with soap and water. The hands of non-shooters as well as automobile brake repair workers were also sampled to test if false-positives could also arise.

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Additionally, two sampling approaches were tested, pressing a small piece of adhesive tape against the dorsal region of the hands of shooters and using a polymeric resin. Both sampling methods showed the same efficiency for removing the GSR from the hands; however, due to the time required for resin polymerization, and the irregular morphology of the resin that complicates the analysis, the authors recommended the use of the adhesive tape. Averaged spectra of 20 laser shots of each adhesive tape were treated using Soft Independent Modeling of Class Analogy (SIMCA) pattern recognition method. The shooters and non-shooters were corrected classified, even after washing their hands with soap. Although no false-negative results were found, a false positive result was obtained from one of the samples taken from an automobile brake repair worker.

The occurrence of environmental and/or occupational false-positive tests for GSR using the emission line of Ba was studied by Dockery et al. [17]. LIBS spectra obtained from samples collected using the tape-lift technique from welding, pyrotechnics, key cutting, mechanics, and paper product occupations or simulations, were compared with the one collected from the hands of a shooter producing significant false positive results. These findings highlight the importance of performing multi-elemental analysis.

Hondrogiannis et al. [18] explored the ability to identify GSR from the inside of cartridge casings using a commercial field-portable LIBS system and to link the elements measured with the ammunition manufacturer. The GSR particles were collected from the fired cartridges by swabbing with cotton swabs. Then, the swab was placed in the LIBS sample chamber and ablated with multiple shots at different swab locations. Although they detected several elements (including Ba and Sn) the mathematical model generated was not able to unequivocally identify the ammunition manufacturer (classified with 67% accuracy). This result may be due to the similar composition of the primers present in the different ammunition cartridges.

The combined use of Gas Chromatography coupled to Mass Spectrometry (GC-MS) and LIBS was recently proposed for the characterization of both organic and inorganic GSR compounds [19]. The hands of shooters and non-shooters were sampled using cotton swabs. First, a headspace extraction of volatile organic compounds using capillary microextraction of volatiles was performed, followed by the liquid extraction

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of the inorganics. Due to the possibility of obtaining false-negatives (e.g. due to the lower detectability of Sb), the authors proposed the sequential analysis of the same swab by both techniques.

These investigations support the use of LIBS as a fast and relatively inexpensive screening technique for GSR detection; for example, to differentiate shooters and non-shooters or to investigate the period of time that a shooter will test positive for GSR. Despite these findings, no attempts have been made to visualize the GSR patterns by LIBS imaging. Therefore, and due to the mentioned need for alternative methods capable of furnishing simultaneous elemental analysis of higher specificity for GSR, we investigate the use of LIBS to reveal the Pb, Sb, and Ba firing patterns on clothing targets. First, the simultaneous multielemental analysis of individual macroscopic GSR particles were performed in order to investigate the LIBS conditions under which the GSR patterns can be visualized. Then, cotton cloths targets that were shot with conventional ammunitions at different distances were measured. Since in the forensic field the preservation of the forensic evidences is required, the LIBS imaging analyses were carried out on a specific support, where the GSR patterns were previously transferred. Therefore, the integrity of the clothing targets is assured being possible further forensic tests.

## 2. Experimental

### 2.1. Ammunition and firearms

Three different 9 x 19 mm conventional ammunition cartridges were fired at 0.5 m from the target. Two full metal jacket (FMJ) ammunitions manufactured by Santa Barbara (Spain), called SB-T 93+ and SB 96+, and one semi-jacketed hollow point (SJHP) ammunition manufactured by Sellier&Bellot (Czech Republic), called S&B. Then, S&B cartridges were also fired at 30, 50, and 150 cm distances from the target. White cotton cloths of 20 cm × 20 cm size fixed in cardboards were used as targets. Shots were performed in a shooting gallery with a semi-automatic Glock 17 pistol (Glock Ges.m.b.H., Austria)

### 2.2. Sample collection

To study the capability of LIBS technique to analyze GSR macroscopic particles, 5 to 10 GSR macroscopic particles from each different ammunition were measured. The

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particles were collected from the clothing targets using metal tweezers, and then placed on a double-side tape already fixed to a glass slide. Then, a study aiming at visualizing the GSR patterns using the most representative elements present in the residues of conventional ammunitions was performed. One of the conditions set out to obtain the GSR patterns in the cotton cloth was the preservation of the clothing in order to maintain this evidence for further forensic examination. Since LIBS analysis could destroy the clothing surface due to the high number of laser shots required to perform an imaging analysis, it was needed to transfer the GSR particles to another support. Therefore, a double side adhesive sheet was previously fixed in an aluminum plate (15 cm × 18 cm) that acted as rigid support. The rigid holder was pressed over the clothing, causing the transferring of the GSR pattern to the adhesive support.

### 2.3. Experimental Set-up

The LIBS experimental set-up employed (Figure 1) consisted in a Nd:YAG NL301HT laser (EKSPLA, Vilnius, Lithuania) operating at 1064 nm, with a pulse duration of 4.5 ns. The laser pulse energy was set to 100 mJ/pulse using an attenuator (LOTIS-TII, Minsk, Belarus), and the laser repetition rate was fixed at 5 Hz. The laser pulse was redirected and focused by a mirror (10QM20HM.15 from Newport, Irvine, CA, USA) and a focusing objective (LMH-5X-1064 from Thorlabs, Newton, NJ, USA). Just below this focusing objective, a glass slide was placed in order to protect it from the ejected particles. According to our results, this slide could endure at least $10^4$ shots before being replaced. The attenuation of the laser energy due to the glass slide is compensated by setting higher energy pulse with the attenuator.

The available spectrographs in our laboratory restricted their wavelength range to spectral windows of a maximum of 30 nm; limiting, in consequence, the multielemental and simultaneous capabilities inherent of LIBS analysis. To solve this drawback, the light emitted by the plasma was collected by two different spectroscopic systems to record the spectra at two different wavelength ranges simultaneously. To direct the light to the first system, the plasma emission was focused into an optical fiber, placed with an angle of 45º with respect to the laser beam, using a combination of fused silica plano-convex lenses (Newport SPX022AR.10 and Thorlabs LA4148, lenses 1 and 2 in Figure 1). The light was then introduced through the optical fiber (SR-OPT-8014 from Andor Technology, Belfast, Northern Ireland) into a Czerny-Turner spectrometer (Shamrock

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SR-500i-D1 from Andor Technology) (spectrograph 1, Figure 1) with a focal length of 500 mm and a grating of 1200 lines/mm. Emission signals were finally recorded using an Andor iStar iCCD (iCCD 1, Figure 1) with 1024×1024 pixels having an effective size per pixel of 19.5 μm × 19.5 μm. This configuration of the experimental set-up allowed simultaneous spectra acquisition with spectral width of about 30 nm.

The plasma emission towards the second spectroscopic system followed the same path than the laser beam through the objective and the mirror. The transmittance of the mirror for the investigated wavelength range was almost 100%. Then the light was focused using a fused silica plano-convex lens (lens 3, Figure 1) in a second optical fiber (LG-455-020-3 from Princeton Instruments, NJ, USA). The other end of the optical fiber was fixed to a 0.5 m spectrograph (spectrograph 2, Figure 1) (SpectraProR-500, Princeton Instruments, NJ, USA), which operated with a grating of 2400 lines/mm. The detector was a PI-MAX iCCD camera (iCCD 2, Figure 1) and a ST-133 camera controller (both from Princeton Instruments). This configuration allowed the acquisition of spectral windows with a spectral width of about 15 nm.

The synchronization between the laser shot and both spectroscopic systems was achieved acting the laser as master, and using its trigger output signal as trigger input for both spectrographs

Sample movement for imaging was done using a motorized X-Y stage. The stage is composed by 2 linear stages (VT_80200-2SM; PImiCos GmbH, Eschbach, Germany) with a travel range of 200 mm and a resolution of 0.5 μm. The stage movement velocity was set to 4 mm/s. LIBS mapping required approximately in 2 h 45 min per sample at this experimental conditions.

### 2.4. Data treatment

In a first step, the GSR patterns were generated using an intensity based color scale, referencing the net area of the atomic emission lines under study, at each point of the clothing target. The net areas under the selected lines for each element (283.3 nm for Pb I, 259.8 nm for Sb I, and 455.4 nm for Ba II), after subtracting the signal background, were used. The color scale selected is constant for each element. The maximum value in the scale was chosen to be the percentile 99 for the firing distance of 30 cm for each

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element. The minimum value corresponds to the mean of the analytical signal of the blank samples plus one standard, analyzed in 5 different positions. Area integration of the emission lines was carried out using the "LA/LIBS data analysis software" by Applied Spectra (Fremont, CA, USA) and the maps were built using OriginPro 9.0 by Origin Lab Corporation (Northampton, MA, USA).

## 3. Results and Discussion

### 3.1 LIBS spectra of GSR particles

First, the capability of detecting Pb, Sb and Ba on one single macroscopic GSR particle with only one laser shot was investigated. The analytical emission lines for the three elements of interest were selected in order to get at least one line, free of interferences, of two different elements in the same spectral window; and with enough intensity to be easily detected. For this purpose, the spectral regions between 258-289 nm and 446-463 nm were selected. The spectral lines chosen for the Pb, Sb and Ba, which lie in the mentioned regions, were identified considering the NIST database [20]. Individual GSR macroscopic particles produced by three different ammunitions (SB-T 93+, SB 96+, and S&B) were then analyzed by focusing the laser on them. In order to facilitate the measurements, the particles were previously collected from the clothing using metal tweezers, and then placed on a double-side tape previously fixed in a glass slide. The delay time and the gate width in these LIBS measurements were optimized to be 2 μs and 30 μs, respectively, for the Andor detection system (spectral region of 258-289 nm); and 1 μs and 30 μs for the Princeton detection system (spectral region of 446-463 nm). The spectra of the individual GSR macroscopic particles recorded simultaneously for the two spectral regions are shown in Figure 2 and Figure 3. The particles measured for each ammunition showed similar spectra in terms of composition and intensity. In addition, the spectrum of the adhesive sheet where the GSR particles were deposited was also obtained. The spectral region between 258-289 nm (Figure 2) shows the presence of several lines of two of the three elements of interest, Sb and Pb, as well as other emission lines from Mg, Si, Fe and Sn, for the three GSR particles. Comparing these spectra with the one obtained for the adhesive sheet can be concluded that the presence of Mg is due to the adhesive sheet, but the emission lines of the elements of interest are not interfered. The spectral region between 446-463 nm (Figure 3) shows the presence of an intense emission line of Ba II at 455.5 nm, and a weak line attributed

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to the contribution of Sn I and Ba II emission lines at 452.5 nm. In this spectral region the adhesive sheet does not introduce any interferences in the GSR particle spectra.

Regarding the possibility to differentiate the GSR particles analyzed, it can be observed that the spectrum measured from the S&B ammunition present differences in comparison with the ones measured for the GSR particles of SB-T 93+ and SB 96+ samples. In particular, Al emission lines are only present for the S&B sample. In the case of SB-T 93+ and SB 96+ GSR particles, differences in intensity of the emission lines of Si (Si I, 288.2 nm) and Sn (Sn I, 284.0 nm) allows to differentiate them, in principle. However, these results should be interpreted with caution due to: (i) the low number of ammunitions analysed, (ii) only one shot per ammunition and distance was performed, (iii) the fact that GSR particles are not homogeneous in terms of composition and element concentration (e.g. particles consisting of a single element such as Pb particles can be found separated from the particles with more than one element, like the characteristic Pb-Sb-Ba particles of conventional ammunition), (iv) the powder and/or the primer used by a manufacturer may be shared by several models or several manufacturers, and (v) LIBS cannot unequivocally identify GSR particles, as scanning electron microscopy coupled with energy dispersive spectroscopy (SEM−EDS) does.

Considering the spectra obtained, the emission lines at 259.8 nm of Sb I, 283.3 nm of Pb I, and 455.4 nm of Ba II were selected to visualize the GSR patterns in further studies.

### 3.2 LIBS imaging of targets

The results obtained for the multielemental analysis of individual GSR particles showed the potential capability of LIBS for the identification of Pb, Sb, and Ba on the samples. Therefore, the mapping of the clothing targets shot was also performed to determine the distribution of Pb, Sb, and Ba that will provide a lot of useful information to determine the dispersion of the GSR particles on the clothing. First, the methodology applied in this study aims at avoiding the destruction of the clothing to preserve this evidence for further forensic examination. Since LIBS analysis could destroy the clothing surface, due to the high number of laser shots required to perform imaging analysis, it was needed to transfer the GSR particles to another support. For that purpose, double-side

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adhesive sheet, previously fixed to a rigid sheet of aluminum, was pressed over the clothing, transferring the GSR particles to the adhesive sheet without changing the spatial distribution of the particles. Apart from these advantages, this collection approach had the benefit of offering a regular and flat surface that facilitated the LIBS measurement.

After sample collection, the sample holders with the GSR particles were subjected to LIBS analysis using shorter gate widths than those used in the analysis of the individual particles; in particular, the widths were fixed at 10 μs for the spectral region 258-289 nm and 5 μs for the 446-463 nm region. These conditions were selected in order to avoid the detectors saturation when analyzing regions with high GSR particles concentration as it happens around the bullet entry hole. Measurements of an area of 130 mm × 165 mm, resulted in 150 × 207 single shots (31050 spectra for each spectral range were measured). The areas under the selected lines for each element (283.3 nm for Pb I, 259.8 nm for Sb I, and 455.4 nm for Ba II) after subtracting the signal background were used to construct the maps. Figure 4 depicts the LIBS mappings obtained for the distribution of the selected Pb I, Sb I, and Ba II emission lines in the three cotton targets shot with S&B ammunition at distances of 30, 50, and 150 cm, respectively. The entry holes of the bullets are clearly detectable in the nine images due to the higher concentration of Pb, Sb, and Ba elements in the area, result of the bullets wipe. In the three images of the shortest distance (30 cm), around the bullet entry hole, a circular area that decreases in intensity with the distance to the center of the hole is observed. However, this circular area is not so evident in the six images of the two targets shot at larger distances (50 and 150 cm), specially for the Ba analysis. The intensity of the Pb, Sb and Ba detected decreases with the shooting distance, being more evident in the images of the targets shot at 150 cm than in the images of the targets shot at 50 cm. The intensity distributions showed by the three elements for each target are very similar, mainly Pb and Ba distributions at 30 and 50 cm. However, at 150 cm Ba intensities are almost negligible being obtained only slight signals around the bullet entry hole. At this distance the Sb distribution shows some points which could correspond with the presence of some GSR particles dispersed on the sample surface.

The aspects observed in the images, like the bullet wipe residue or the metal particles dispersed, are in line with the usual distribution of the GSR particles at different

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distances observed in the forensic laboratories using colorimetric assays. In fact, the observed elements allow to point out that the first target (30 cm) was shot at near contact range while the other two (50 and 150 cm) were shot at intermediate range or even at distant range. Notwithstanding, to study the similarities and differences of the patterns obtained by LIBS and color tests in a more comprehensive way, it will be necessary to apply both methods to a series of test-firings at varying distances with, also, different ammunitions and firearms.

### 3.3 Sample reanalysis

Reanalysis of samples might be requested for forensic samples; therefore, it is important to investigate if the methodology proposed preserves the samples for further analysis. As it was explained in previous paragraphs, the proposed sample collection methodology aims to preserve the original samples without physical damage but, after the GSR are transferred to the adhesive, LIBS destroys the evidence present in the adhesive as it is necessary to resample the cloth to analyze it again. Theoretically, an important amount of the GSR particles is removed from the target in the transferring process but it is expected that a significant amount of the GSR particles remains in the cotton cloths and, sample reanalysis can be done if needed.

In order to check this, a second analysis was carried out by using the same clothing target fired at 30 cm previously analyzed. The rigid support with adhesive tape was pressed against the target and then its surface was analyzed by LIBS at the same experimental conditions than in previous experiments. Figure 5 show the mappings obtained for Pb, Sb and Ba for this second analysis. Although the intensity measured in this new analysis is lower than the obtained in the first one, a broad distribution of the Pb, Sb, and Ba elements around the bullet entry hole, which follows an analogous pattern that in the first analysis can be still observed.

## 4. Conclusions

Several potential applications of LIBS in GSR detection, such as the possible differentiation between shooters and non-shooters or estimations of the period of time that a shooter will test positive for GSR have already been reported in the literature. In the present work, it has taken a further step forward with the visualization of GSR patterns by LIBS imaging.

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The LIBS set-up employed in these experiments, based on the simultaneous use of two spectrographs and iCCD cameras, allowed the acquisition of spectra from two different wavelength regions (258-289 and 446-463 nm). The main benefit of using two spectral ranges at the same time was the multielemental detection of the characteristic elements Pb, Sb, and Ba present in the GSR particles from conventional ammunition, as well as others (such as Mg, Si, Fe and Sn) that can offer additional information. These results were confirmed when individual macroscopic GSR particles were analyzed. On the three types of ammunitions tested, the three of them were distinguished based on composition (one of the ammunitions presented Al emission lines while others were not) or by differences in intensity (differences of the emission lines of Si and Sn were observed on the two ammunitions with the same GSR elemental composition). However, the results obtained in this work must be considered as exploratory, and therefore, they cannot be extrapolated to other GSR particles or manufactures due to, along with other factors, the low number of different cartridges analyzed.

The surface where the GSR particles pattern was transferred, was a double-adhesive sheet fixed on a plate of aluminum. The analysis of the adhesive sheet showed no interferences with the GSR particle spectra, probing the suitability of the transference method proposed. Additionally, this sample holder has great advantages, facilitating the sample collection and the analysis by LIBS offering a rigid and flat surface.

The LIBS mapping of the targets shot from three different distances showed the spatial distribution of Pb, Sb and Ba over the clothing targets. The results obtained probed the high potential of LIBS to visualize the GSR patterns. Also, a second analysis of samples showed that, although an important amount of the GSR particles is removed from the target in the transferring process, a significant amount of the GSR particles remains allowing the sample reanalysis if needed.

Although in this work targets shot with conventional ammunitions were analyzed, the multielemental detection by LIBS can also be used to reveal the patterns produced from other types of ammunition (e.g. lead-free ammunition or tagged ammunition) by previously selecting the spectral range of interest or using a LIBS set-up that covers a wider spectral range. Additionally, the presence of other compounds in the samples, such as blood or mud, should be considered for the application to real samples. The use

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of LIBS to reveal the GSR patterns show great advantages over tests based on color chemical reactions such as the possibility of multi-elemental analysis, which increase the specificity and prevents potential false-positives. Further advantages are the fact that the sample can be analyzed in less than 3 hours, time that can be reduced by half with a fully automated detection system, with no sample preparation and not requiring hazardous chemicals for sample preparation. However, and although the cost per LIBS analysis is negligible, the cost of LIBS instrumentation is considerably higher than color test, and also, LIBS require instrumental knowledge.

Finally, it should be underlined that the LIBS methodology proposed is effective to visualize the GSR patterns for shooting distance estimation and offers additional information in terms of general GSR composition. However, LIBS is not recommended for single particle identification and cannot compete with SEM−EDS, which is acknowledged as the most specific method for GSR identification due to its ability to identify GSR particles on the basis of their characteristic morphology and elemental composition.

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**Figure captions.**

**Figure 1.** LIBS experimental set-up.

**Figure 2.** LIBS spectra of individual GSR particles of SB-T 93+, SB-T 96, and S&B ammunition and the adhesive sheet at 258-289 nm spectral region. LIBS parameters: 1064 nm Nd:YAG laser; 4.5 ns, pulse duration; 100 mJ/pulse, laser energy; 2 μs delay time 30 μs gate . Emission lines selected to obtain the GSR patterns in bold.

**Figure 3.** LIBS spectra of individual GSR particles of SB-T 93+, SB-T 96, and S&B ammunition and the adhesive sheet at 446-463 nm spectral region. LIBS parameters: 1064 nm Nd:YAG laser; 4.5 ns, pulse duration; 100 mJ/pulse, laser energy; 1 μs delay time and 30 μs gate. Emission lines selected to obtain the GSR patterns in bold.

**Figure 4.** LIBS mappings of the distribution of Pb (λ= 283.3 nm, Pb I), Sb (λ=259.8 nm, Sb I) and Ba (λ=455.4 nm, Ba II) in cotton targets shot with S&B ammunition at distances of 30, 50, and 150 cm.

**Figure 5.** LIBS mappings of the distribution of Pb (λ= 283.3 nm, Pb I), Sb I (λ=259.8 nm, Sb I) and Ba (λ=455.4 nm, Ba II) obtained after the second transferring process of the target fired at 30 cm distance with S&B ammunition.

FIGURE 1

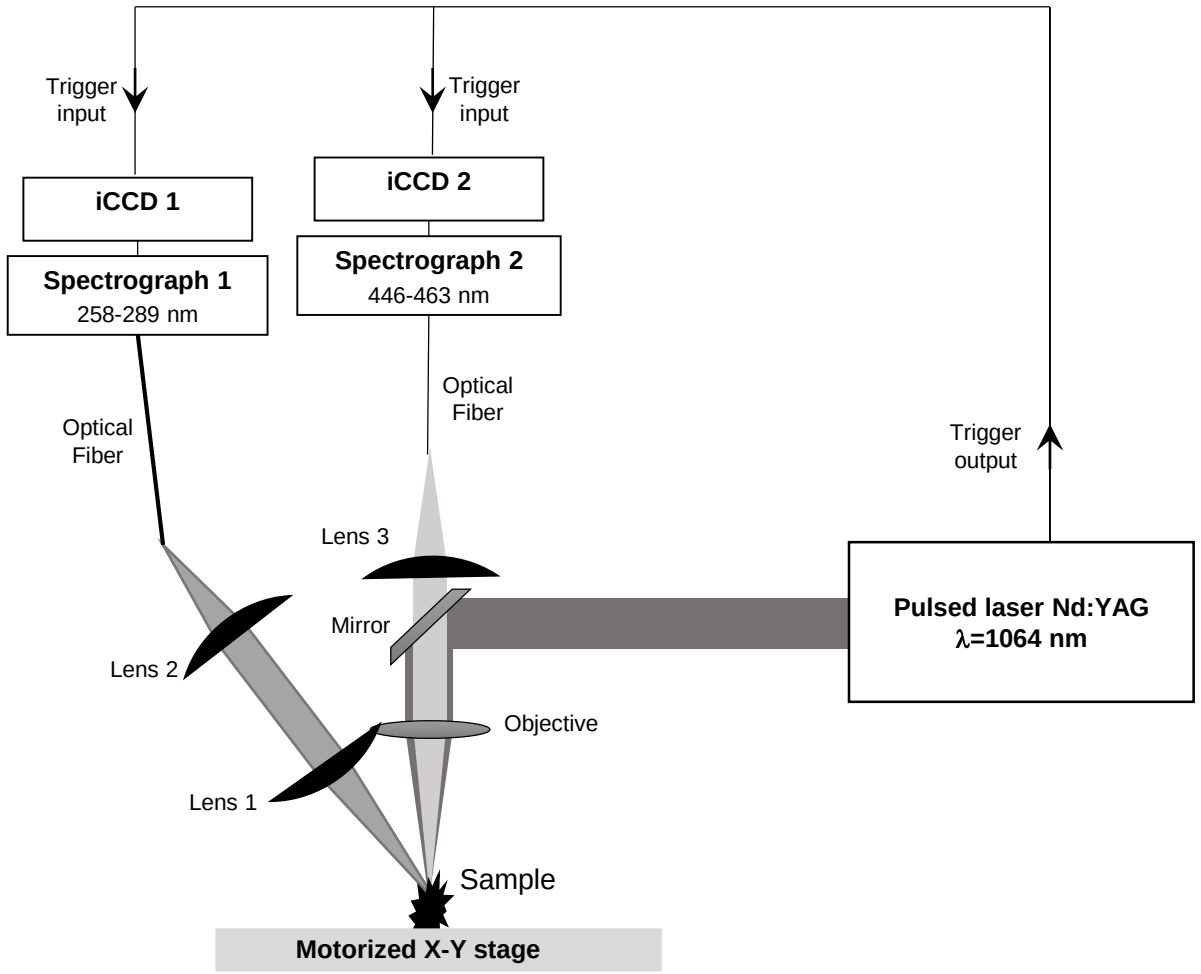

Trigger input
Trigger input
iCCD 1
iCCD 2
Spectrograph 1
258-289 nm
Spectrograph 2
446-463 nm
Optical Fiber
Optical Fiber
Trigger output
Lens 3
Mirror
Pulsed laser Nd:YAG
λ=1064 nm
Lens 2
Objective
Lens 1
Sample
Motorized X-Y stage

FIGURE 2

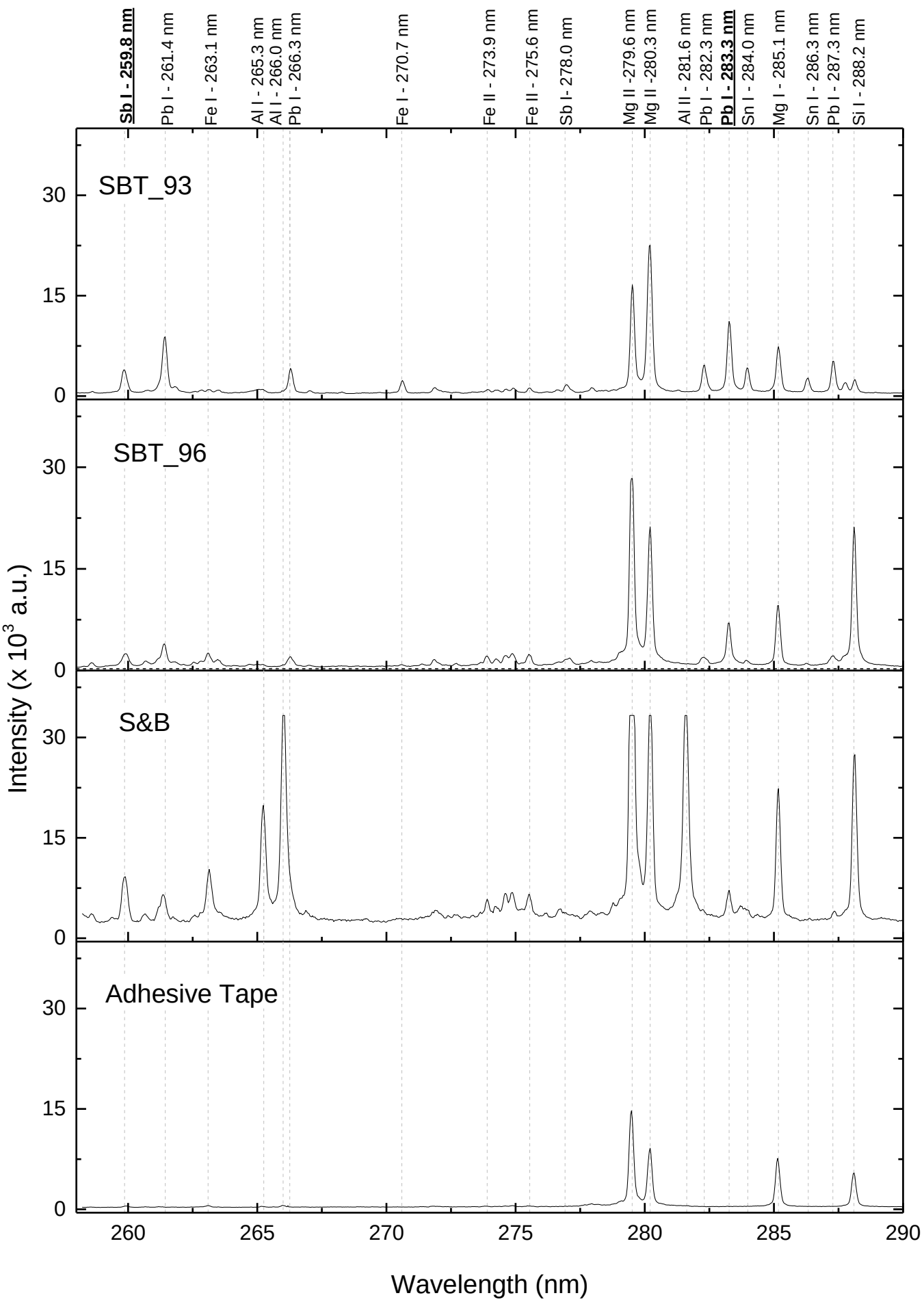

Sb I - 259.8 nm
Pb I - 261.4 nm
Fe I - 263.1 nm
Al I - 265.3 nm
Al I - 266.0 nm
Pb I - 266.3 nm
Fe I - 270.7 nm
Fe II - 273.9 nm
Fe II - 275.6 nm
Sb I - 278.0 nm
Mg II -279.6 nm
Mg II -280.3 nm
Al II - 281.6 nm
Pb I - 282.3 nm
Pb I - 283.3 nm
Sn I - 284.0 nm
Mg I - 285.1 nm
Sn I - 286.3 nm
Pb I - 287.3 nm
Si I - 288.2 nm
SBT_93
SBT_96
S&B
Adhesive Tape
Intensity (x 10^3 a.u.)
Wavelength (nm)
0
15
30
260
265
270
275
280
285
290

FIGURE 3

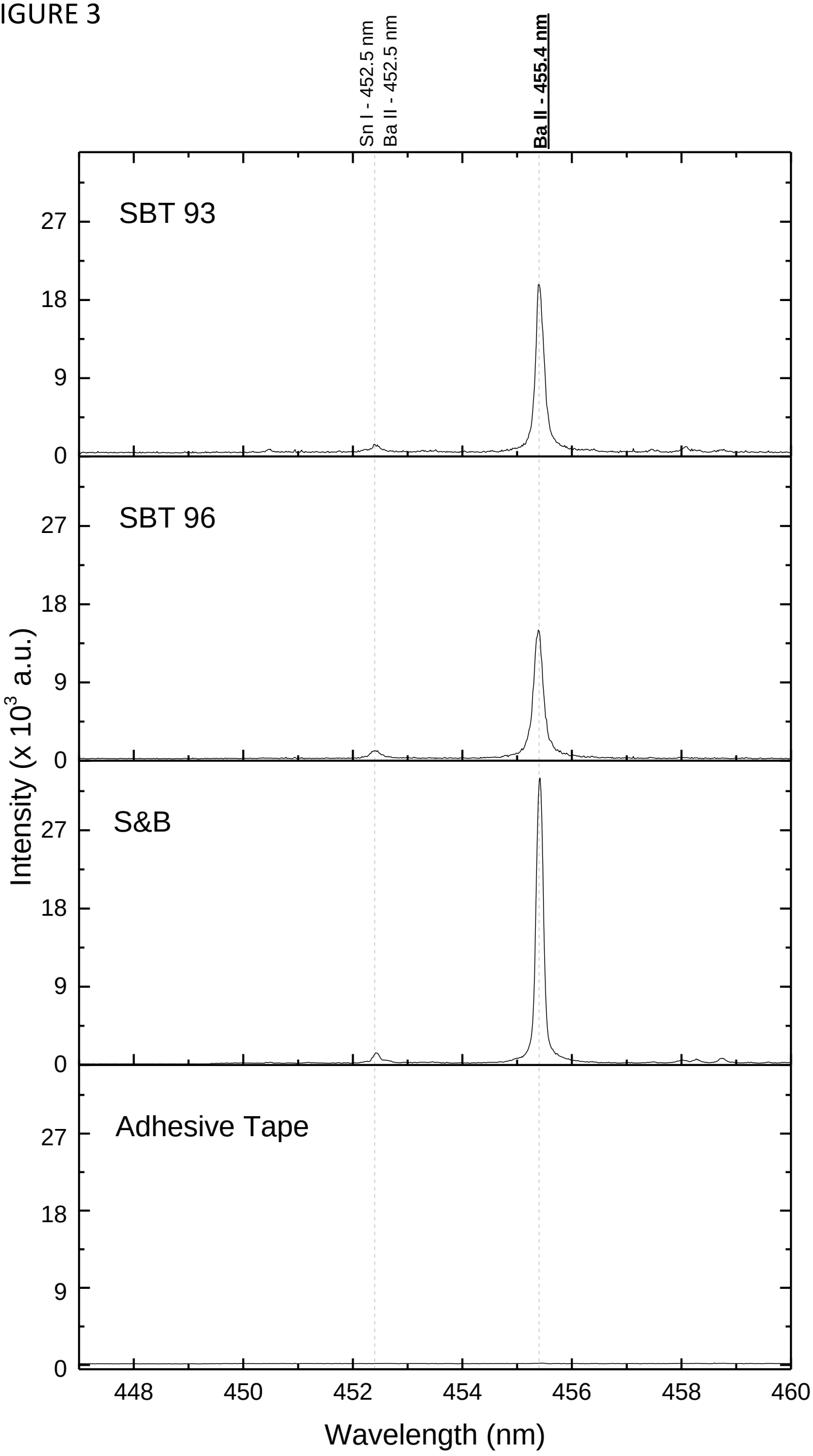

Sn I - 452.5 nm
Ba II - 452.5 nm
Ba II - 455.4 nm
SBT 93
SBT 96
S&B
Adhesive Tape
Intensity (x 10^3 a.u.)
0
9
18
27
448
450
452
454
456
458
460
Wavelength (nm)

FIGURE 4

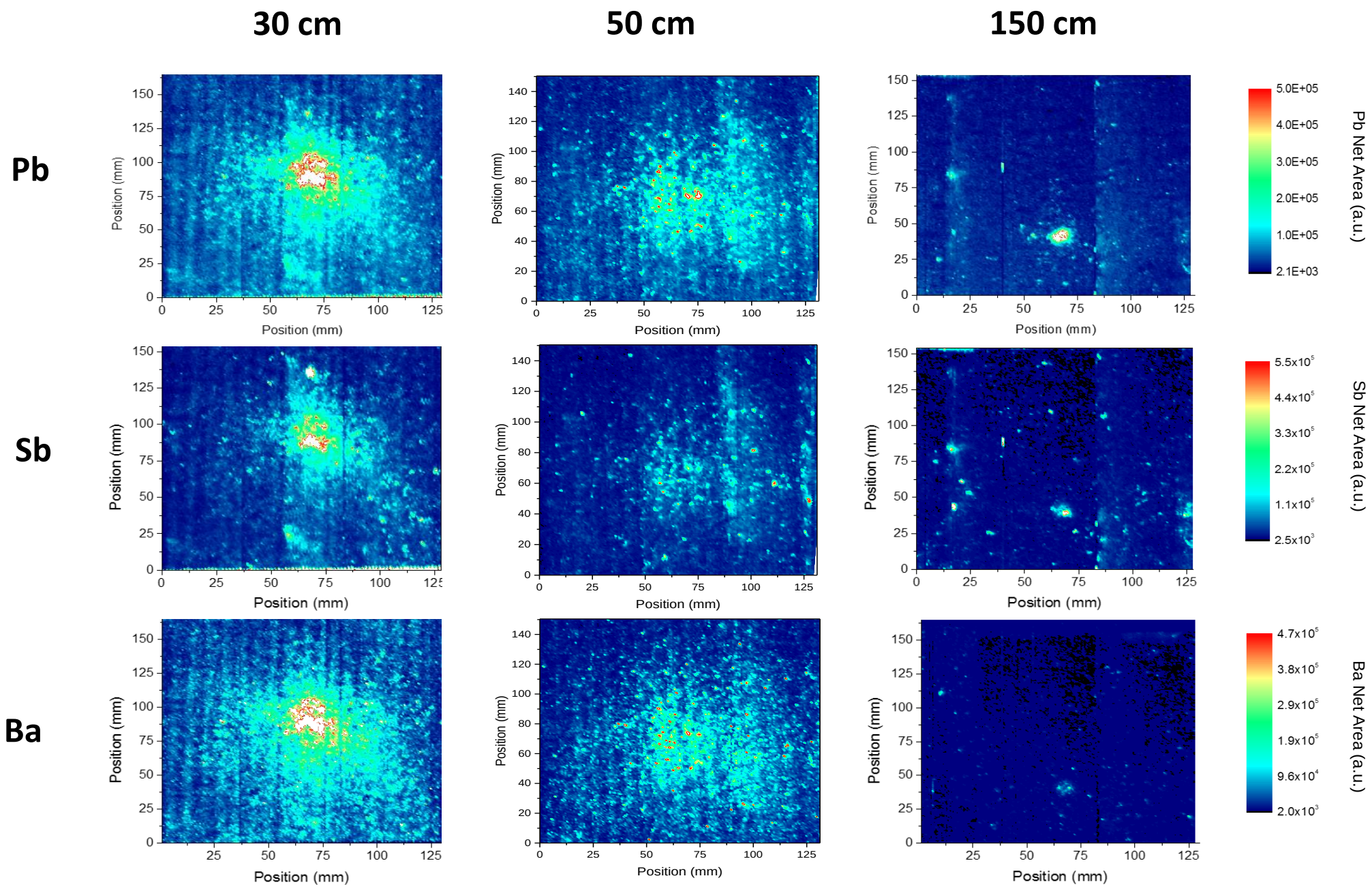
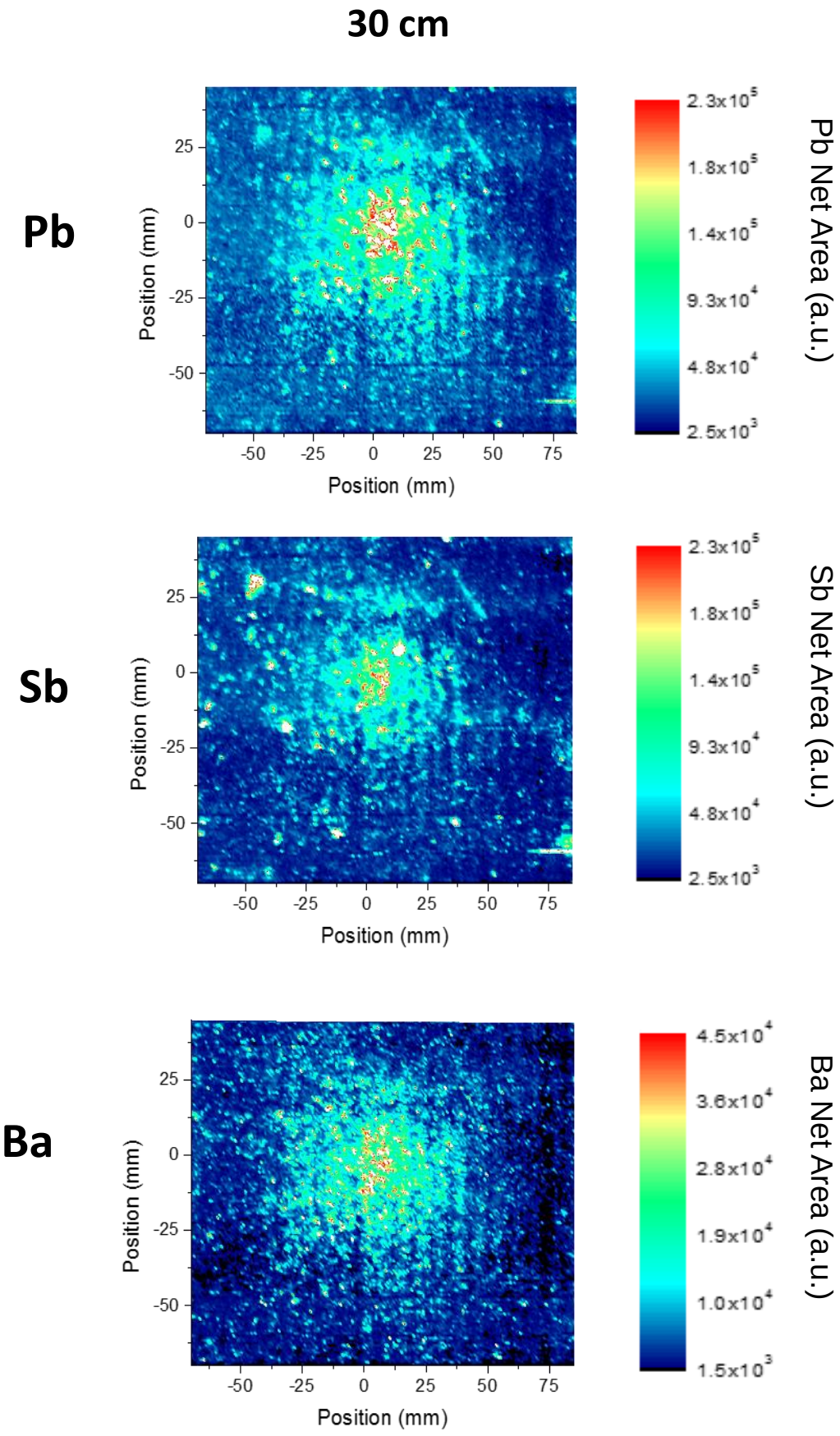

30 cm
50 cm
150 cm
Pb
Sb
Ba
Position (mm)
Pb Net Area (a.u.)
5.0E+05
4.0E+05
3.0E+05
2.0E+05
1.0E+05
2.1E+03
Sb Net Area (a.u.)
5.5x10^5
4.4x10^5
3.3x10^5
2.2x10^5
1.1x10^5
2.5x10^3
Ba Net Area (a.u.)
4.7x10^5
3.8x10^5
2.9x10^5
1.9x10^5
9.6x10^4
2.0x10^3

FIGURE 5


30 cm
Pb
Position (mm)
Position (mm)
2.3x10^5
1.8x10^5
1.4x10^5
9.3x10^4
4.8x10^4
2.5x10^3
Pb Net Area (a.u.)
Sb
Position (mm)
Position (mm)
2.3x10^5
1.8x10^5
1.4x10^5
9.3x10^4
4.8x10^4
2.5x10^3
Sb Net Area (a.u.)
Ba
Position (mm)
Position (mm)
4.5x10^4
3.6x10^4
2.8x10^4
1.9x10^4
1.0x10^4
1.5x10^3
Ba Net Area (a.u.)