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PAPER

CRIMINALISTICS

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Detection of Gunshot Residue in Blowfly Larvae and Decomposing Porcine Tissue Using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)*

ABSTRACT: Blowfly larvae and porcine tissue contaminated with gunshot residue (GSR) were collected during summer and winter months, over a 37-day and a 60-day sampling period, respectively. Wound samples were microwave-digested and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for the detection of antimony, barium, and lead. During summer, the 37-day sampling period encompassed all stages of decomposition, except skeletonization. The three elements were detected in larvae only on days 3 and 4 after death but were detected at significant levels in tissue samples throughout the entire sampling period. In winter, no significant decomposition was observed throughout the 60-day sampling. Although temperatures were too low for blowfly activity, the three elements were detected in the tissue samples at relatively constant, significant levels. Hence, GSR determination in tissue was more dependent on decomposition stage rather than time since death.

KEYWORDS: forensic science, gunshot residue, inductively coupled plasma mass spectrometry, scanning electron microscopy/energy dispersive spectroscopy, microwave digestion, blowfly larvae

Characteristics of gunshot wounds can vary greatly based on the type of firearm, the firing distance, the type of ammunition, and the location of the wound. Such variability is further influenced by many postmortem factors, including bodily decomposition, burial, and insect activity in and around the wound tract. Decomposition and burial can obscure obvious gunshot residue (GSR) tattooing or stippling while insect activity can create new tracts, obscure existing tracts, and subsequently change the morphology of the wound. Hence, identification of gunshot wounds, particularly in decomposing corpses, is complicated, and the ability to chemically detect and identify GSR around a suspected gunshot wound would be a valuable tool.

Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) is currently the most common technique for the detection of GSR because it combines a morphological examination with elemental analysis (1). GSR particles are typically collected from shooters' hands or surfaces using an adhesive tab mounted on an aluminum stub. This method was shown to be the most efficient collection technique by DeGaetano et al. (2) when compared with glue lifting and concentrating procedures. SEM is used to locate spheroid particles on the adhesive tab with a diameter of approximately 10 microns. An EDS spectrum is then taken to identify elements present in the particle.

Wolten et al. (3) demonstrated four elemental combinations that were observed only in GSR particles and hence were labeled as "characteristic" of GSR. The most prominent of these combinations was lead (Pb), barium (Ba), and antimony (Sb). A recent study by Torre et al. (4) demonstrated that certain types of brake pads contain particles with Pb, Ba, and Sb. However, these particles also contained significant levels of iron and lacked the characteristic spherical morphology of GSR particles.

Despite the obvious advantages of SEM/EDS, the technique is not without limitations. Samples are typically collected using an adhesive stub that is dabbed across the sample surface. However, with successive dabbings, particles may become embedded in the adhesive layer which can prevent detection in the subsequent analysis (5). Furthermore, any debris on the sample surface can hamper particle visualization (6). When the SEM electron beam interacts with the stub, local heating effects cause vaporization of more volatile components, causing distortion of the stub surface and potentially displacing particles of interest (5). While modern instruments are capable of automated searches, the analysis is still time consuming, taking up to several hours per cm^2 of sample (7).

More recently, inductively coupled plasma mass spectrometry (ICP-MS) has been used for the determination of antimony, barium, and lead in GSR as well as for differentiating bullets according to elemental composition (8–12). Koons demonstrated the potential of ICP-MS for GSR identification with the analysis of cotton-tipped swabs spiked with Sb, Ba, and Pb (10). Instrument detection limits for the three elements were at least one order of magnitude less

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than the levels associated with GSR (40–500 ng) and were superior to corresponding detection limits for flameless atomic absorption and ICP-atomic emission spectroscopy (AES).

Rather than determining GSR on surfaces or in tissue samples, Roeterdink et al. (13) investigated the possibility of detecting GSR in larvae feeding on beef into which test shots had been previously fired. Larvae were digested in nitric acid on a hot-plate, and levels of Sb, Ba, and Pb in the digests were successfully determined by ICP-MS. This unique approach has potential for detecting GSR in cases where the visual assessment of gunshot wounds is problematic. However, the study was conducted indoors under controlled conditions using beef contaminated with GSR and hence an outdoor study using larvae collected from decomposing tissue is warranted.

As far as the authors are aware, no literature is available in which ICP-MS is used to detect GSR in decomposing tissue samples or larvae feeding on decomposing tissue. However, the technique has great potential in such cases as ICP-MS is neither limited by discoloration because of decomposition nor by larval activity that can alter the appearance of the wound (13).

In this research, the potential of ICP-MS for the determination of Sb, Ba, and Pb in larvae and porcine tissue samples is investigated. An indoor study was initially conducted to demonstrate detection of the three elements in larvae. Medicinal maggots were deposited on beef contaminated with GSR, and larvae were collected over the course of 9 days. Larvae were microwave-digested and then analyzed by ICP-MS for the presence of Sb, Ba, and Pb. Two outdoor studies were then conducted; one during the late summer (September–October) and one during the winter (January–March). In each study, one pig was shot 11 times and a second, stabbed pig was used as a control. Wound tissue was collected from each pig at the same time interval throughout the sampling period. Larvae were also collected from the wounds when present. GSR and control tissue samples were analyzed initially by SEM/EDS to confirm the presence of GSR. Tissue and larvae samples were prepared for analysis by microwave digestion. This preparation procedure was chosen to enable an efficient digestion of the complex sample matrix. Digests were subsequently analyzed by ICP-MS for the presence of Sb, Ba, and Pb, investigating the persistence of these elements through the decomposition process.

Materials and Methods

Indoor Study

A 2.78 lb round bottom roast, purchased from a local grocery store, was shot eight times with a 9 mm GLOCK™ handgun using 115-grain jacketed hollow point cartridges (American Eagle Federal Cartridge +p+; Federal Cartridge Co., Anoka, MN, Lot # 430399WI40). The GSR contaminated meat was then cut into approximately 1 in. cubes and placed onto a plastic platform in the bottom of a plastic specimen cup (Premium Plastics, Inc., Chicago, IL). Five specimen cups were prepared containing beef that had been shot, and five cups were prepared containing control beef that had not been shot, which were used as controls. A wet paper towel was placed under each platform in the specimen cups to maintain a humid atmosphere. The pieces of meat were also sprinkled with water every day to prevent desiccation. Approximately 20 sterile first instar *Phaenicia sericata* medicinal larvae (Monarch Labs, Irvine, CA) were placed on each piece of beef. These larvae had previously been fed a diet of soy protein and yeast. The cups were covered with two layers of Kimwipes® and secured with a rubber band. For five consecutive days, approximately 10 larvae were collected from a new specimen cup (GSR contaminated and control) and stored at −80°C until analysis.

Outdoor Studies

In late summer (September 2007), two euthanized pigs (approximately 200 lbs each) were obtained from the Michigan State University Swine Research Facility. All animals used in this research were treated in accordance with guidelines set forth by the Michigan State University Institutional Animal Care and Use Committee (IACUC). One pig was shot 11 times with a 9 mm GLOCK™ handgun using 115-grain full metal jacketed cartridges (American Eagle; Federal Cartridge Co., Lot # 430399WI40). The muzzle-to-target distance was 5 cm, and the wounds were spaced approximately 10 cm apart. The firearm was cleaned between shots to prevent carry-over. The pigs were then transported to a research field where the control pig was stabbed 11 times to create wounds to attract blowflies. The pigs were covered with mesh tents to prevent predation while still allowing exposure to the elements. The process was repeated in the winter (January 2008) with another two pigs and all other parameters were kept constant.

In the summer study, the 11 wounds from the shot and stabbed pigs were collected over the course of 37 days. A circular tissue sample of the skin and underlying fat was excised in an approximately 4 cm radius around the wound, wrapped loosely in wax paper, sealed in a plastic freezer bag, and stored at −80°C until analysis. Blowfly larvae were collected directly from the wounds on both the stabbed and shot pigs on 10 different days between days 3 and 15 after death. The larvae were sealed in plastic freezer bags and stored at −80°C until analysis. For the winter study, wounds were collected in the same manner over the course of 60 days. However, no larvae were collected during the winter study because of the low temperatures that prevented blowfly activity.

SEM/EDS Analysis

Tissue samples collected on days 1, 2, 5, and 8 in the summer study were dabbed 100 times with adhesive carbon tabs (SPI® Supplies; West Chester, PA) and viewed using a JEOL 6400V SEM (JEOL Ltd., Tokyo, Japan) with LaB_6 emitter coupled with an INCA EDS detector (Oxford Instruments, Oxfordshire, United Kingdom). The accelerating voltage was 20 kV, and the working distance was 15 mm. The tissue samples were manually scanned for spheroid particles with a diameter >10 μm, and for such particles, EDS spectra were collected over the entire particle to identify the presence of Sb, Ba, and Pb.

Microwave Digestion of Larvae and Tissue Samples

Larvae and tissue samples were thawed prior to digestion. For larvae samples, approximately 0.03–0.50 g larvae was placed into a quartz vessel (Milestone, Inc., Shelton, CT). For tissue samples, the skin was separated from the underlying fat and connective tissue using a scalpel and then 0.30–0.90 g of the prepared tissue was placed into a quartz vessel. Two milliliters of Optima grade HNO_3 (Fluka, Buchs, Switzerland) and 1 mL H_2O_2 (CCI, Columbus, WI) were then added to each vessel. The vessels were placed inside a Teflon® reaction vessel (Milestone, Inc.) that contained 10 mL high-purity H_2O (Honeywell Burdick & Jackson, Muskegon, MI) and 2 mL H_2O_2. Procedural blanks were prepared in the same manner, omitting the larvae or tissue samples. Vessels were sealed per the manufacturer's instructions and digested in a microwave digestion unit (Ethos EX, Milestone, Inc.) using the following

digestion program: 15 min ramp from ambient temperature to 210°C and held at 210°C for 10 min. Following digestion, the reaction vessels were cooled to approximately 95°C before opening. A 0.5-mL aliquot of the digest was then diluted with high-purity H_2O to yield a final concentration of 2% HNO_3.

ICP-MS Analysis of Larvae and Tissue Samples

Thirteen multi-element calibration standards containing Sb, Ba, and Pb were prepared from stock standards of each element (1000 μg/mL each, SPEX CertiPrep, Inc., Metuchen, NJ). The solutions were diluted with 2% HNO_3 to yield concentrations ranging from 0.10 ng/mL to 500 ng/mL of Sb, Ba, and Pb. Each standard was spiked with 20 ng/mL indium (In) and 20 ng/mL bismuth (Bi) (SPEX CertiPrep, Inc.), both of which are routinely used as internal standards in our laboratory. Prior to analysis, the digest solutions and procedural blanks were also spiked with 20 ng/mL In and 20 ng/mL Bi as internal standards.

Calibration standards and digest solutions were analyzed by ICP-MS using a Micromass Platform quadrupole ICP-MS (Thermo Fisher Scientific, Inc., Waltham, MA). The instrument is equipped with a hexapole collision cell, a Dynolite™ detector with a -15 kV conversion dynode and photomultiplier tube, and a CECTAC ASX-500 autosampler (CETAC Technologies, Omaha, NE). Instrument operating parameters are given in Table 1. The instrument was operated in selected ion monitoring (SIM) mode for ^{121}Sb, ^{138}Ba, and ^{208}Pb using MassLynx software (version 3.4; Thermo Fisher Scientific, Inc.).

Calibration standards were analyzed in triplicate in order of low to high concentration to minimize carry-over effects. Digest samples and procedural blanks were analyzed in triplicate in the following order: procedural blanks, control larvae digests, control tissue digests, GSR larvae digests, and GSR tissue digests. The GSR tissue digests were analyzed in order of last day of collection to the first day of collection, as it was hypothesized that wounds collected later would contain less GSR than wounds collected earlier in the study. Calibration standards were reanalyzed after every 30–33 samples to minimize error because of instrument drift or memory effects. After sample injection, the injector was rinsed for 3 min with 2% HNO_3, and two additional HNO_3 rinses were performed between groups of samples.

Instrument responses for ^{121}Sb and ^{138}Ba in the calibration standards, tissue digests, and larvae digests were normalized to ^{115}In, while the response for ^{208}Pb was normalized to ^{209}Bi. Concentrations of ^{121}Sb, ^{138}Ba, and ^{208}Pb were then determined from the calibration curve and expressed as μg element/g larvae or tissue, as appropriate.

TABLE 1—*Inductively coupled plasma mass spectrometry operating parameters.*

ICP-MS Operating Parameters	
RF power (W)	1350
Ar flow rates (L/min)	
Outer	13.00
Auxiliary	0.72
Nebulizer	0.71–0.73
Sampling cone	Ni with Cu core, 1.14-mm diameter orifice
Skimmer cone	Ni, 0.89-mm diameter orifice
MS resolution	Unit mass
Data collection parameters	
Mode	Selected ion recording (peak jumping)
Sample scan time (min)	1.25
Dwell time (s)	0.1
Repeats	1
Autosampler parameters	
Sample read delay (s)	105 (1.75 m)
Rinse time (s)	90

Results and Discussion

Indoor Study

First instar *P. sericata* blowfly larvae were placed onto GSR contaminated and control beef, under controlled conditions. By day 2, the larvae were primarily second instars, and by day 3, most were early third instars. Pupae were first observed on day 9. Larvae and pupae samples were digested and analyzed by ICP-MS as described previously. Concentrations of Sb, Ba, and Pb in larvae and pupae feeding on GSR and control tissue are shown in Fig. 1.

Only Ba was observed in the control larvae and pupae and, for all time points, the concentration of Ba was < 1.0 μg/g larvae. For larvae feeding on the shot beef, concentrations of Ba ranged from 10.3 μg/g larvae on day 1 to a maximum of 80 μg/g larvae on day 7. This range in concentration could indicate bioaccumulation of Ba; however, this hypothesis was not tested further. Antimony was detected in the larvae on each day except day 2, with concentrations ranging from 0.15 to 0.75 μg/g larvae. The lack of Sb in larvae collected on day 2 may simply be because of insufficient consumption for detection by ICP-MS. Instrument detection limits were higher for Sb than for Ba or Pb, which will be discussed later. Lead was detected in larvae at all time points—the maximum Pb concentration of 6.26 μg/g larvae was detected on day 1 with concentrations ranging from 1.29 to 0.42 μg/g larvae for subsequent time points.

Outdoor Study Decomposition Observations

The fresh gunshot wounds, inflicted with a firing distance of 5 cm, exhibited typical characteristics of close range gunshot wounds including blackened wound edges and GSR particle deposition in and around the wound. Because the pigs were euthanized prior to the shooting, no stippling was observed, as stippling is an antemortem phenomenon that requires blood flow.

During the sample collection period in the summer study, temperatures ranged from a high of 88.6°F (day 19) to a low of 35.3°F (day 11). Significant rainfall also occurred on days 2, 5, 20, 21, 26, and 35. Bloating was evident in both pigs 1 day after death, and blowfly eggs were observed in the orifices. Many blowfly larvae were present by day 2. Seepage of decompositional fluids was evident by day 4 and pronounced by day 5, indicating the start of active decay. Skin slippage was also observed at that time. Active decay began to slow and was no longer obvious by day 11, indicating the start of desiccation. Blowfly larvae were present in the wounds until day 15 and were found around the carcass until day 17. By day 37, the end of the collection period, the carcasses were almost fully desiccated.

Initially, the stab wounds and gunshot wounds were easily distinguishable (Fig. 2*A*, *D*). However, over the course of the collection period, the wounds became similar in appearance (Fig. 2*B*, *E*) and eventually could not be easily distinguished (Fig. 2*C*, *F*).

In the winter study, temperatures ranged from a high of 54.0°F (day 52) to a low of −5.4°F (day 31). The carcasses were covered with snow on days 5, 8, 12, 16, 26, 30 during the 60-day sampling period. During this study, significant decomposition was not observed; even by day 60, GSR was still visible around the wounds. Although significant bloating was not observed, the beginning of putrefaction was evident.

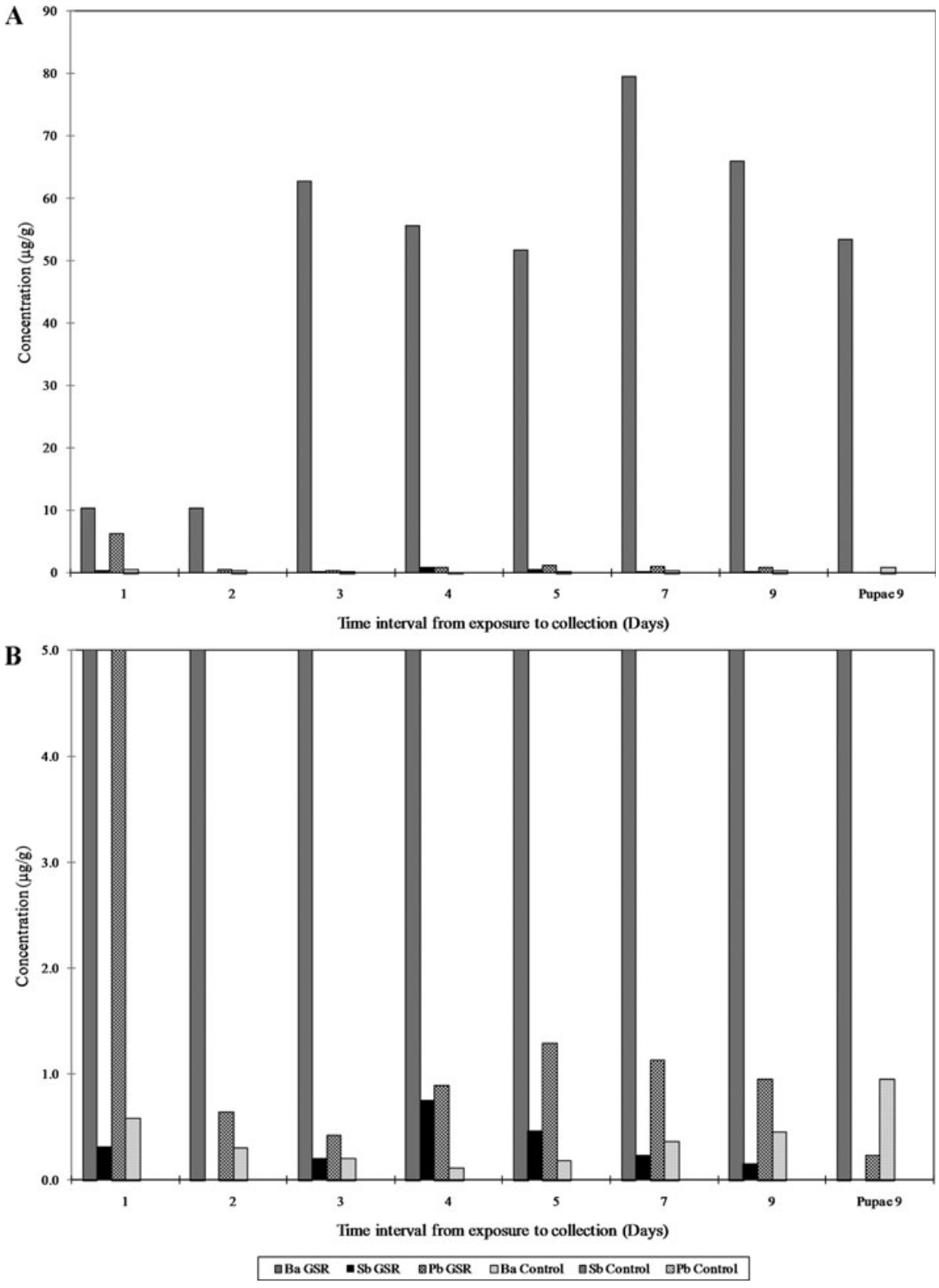

FIG. 1—*Concentration of Sb, Ba, and Pb in larvae and pupae (A) full scale and (B) rescaled to show concentrations at later time points. "Gunshot residue" indicates larvae and pupae feeding on shot beef while "Control" indicates feeding on control beef.*

Outdoor Study SEM/EDS Analysis

Wound samples collected on days 1, 2, 5, and 8 in the late summer study were dabbed 100 times using adhesive carbon tabs and analyzed by SEM. Spheroid particles <10 µm in diameter were subsequently analyzed by EDS to qualitatively identify elements present. Potential GSR particles were observed on the wound collected on day 1. Although other particles were observed, none were deemed to be consistent with GSR because of their crystalline nature and presence of elements such as silicon, potassium, calcium, and chlorine.

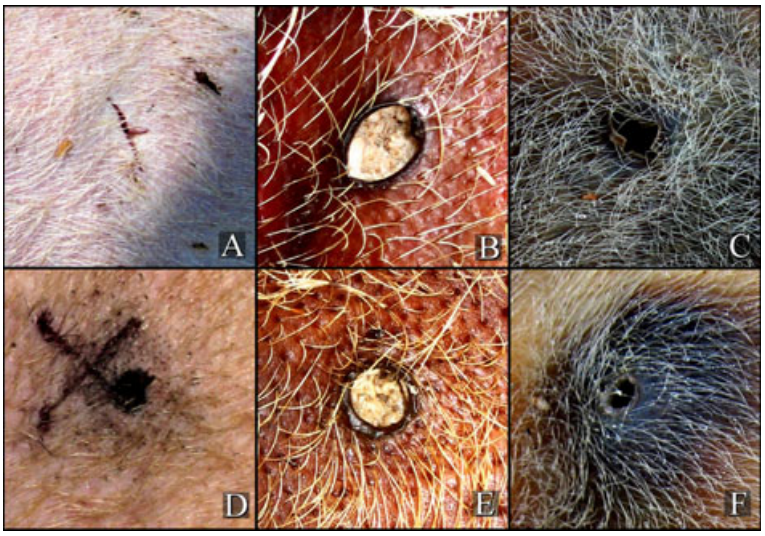

FIG. 2—*Comparison of gunshot residue and stab wounds during summer study. (A) stab wound on day 0; (B) stab wound on day 7; (C) stab wound on day 26; (D) GSR wound on day 0; (E) GSR wound on day 7; (F) GSR wound on day 26.*

Potential GSR particles were not observed on any other wounds collected in the late summer study. There was significant rainfall overnight between days 1 and 2, which likely washed surface GSR from the wounds. Wounds collected after day 8 were not analyzed by SEM/EDS because of the presence of an oily discharge which prevented efficient GSR collection using the adhesive stub method.

Wounds collected on days 1, 2, 5, and 44 during the winter study were also analyzed by SEM/EDS using the procedure described previously. Several likely GSR particles were observed on day 1; SEM images demonstrated the characteristic spherical morphology while EDS confirmed the presence of Sb, Ba, and Pb in the particles. However, similar particles were not observed on days 2, 5, and 44. Again, this may have been because of adverse weather conditions as well as the oily nature of the wounds that prevent efficient collection of GSR particles using the adhesive stub method.

Thus, while SEM/EDS offers specificity in the identification of GSR based on elemental composition and particle morphology, the technique is limited for decomposing tissue samples and appears to be adversely affected by environmental conditions.

ICP-MS Analytical Figures of Merit

Prior to analysis of wound and larvae digests (both for late summer and winter studies), the instrument was calibrated and analytical figures of merit were determined. Linearity over the concentration range 0–500 ng/mL for all three elements was demonstrated *via* triplicate analyzes of the standards. Limits of detection (LOD) were calculated following the method described by Koons (10); that is, the standard deviation for triplicate analyses of the 0 ng/mL standard multiplied by 3 and divided by the slope of the calibration line, which is equivalent to the sensitivity of the instrument. Average LODs were 0.106, 0.074, and 0.017 ng/mL for Sb, Ba, and Pb, respectively. Limits of quantitation (LOQ) were also determined, defined as the lowest concentration of standard in the linear range of the calibration curve. LOQs for Sb ranged from 0.10 to 0.25 ng/mL, from 0.10 to 1.0 ng/mL for Ba, and from 0.10 to 1.0 ng/mL for Pb.

Analytical precision was determined with replicate analysis ($n = 5$) of five digest solutions (one control stab tissue, two samples of GSR tissue, one larvae, and a procedural blank). Average concentrations of Sb, Ba, and Pb in each digest along with the relative standard deviation (RSD) are presented in Table 2. With the exception of Sb in the stab wound sample, all RSDs are < 2.2%, indicating the high precision of the technique. The higher RSD for Sb (6.0%) is likely due to the very low concentrations detected, which were close to the LOQs for that element.

Procedural blanks were prepared and analyzed for both the summer and winter studies. In late summer, concentrations of Sb, Ba, and Pb were below the corresponding LOQs. In winter, concentrations of Sb and Pb were also less than the LOQs. However, the LOQ for Ba was lower than in the previous study and hence Ba was quantified. The average Ba concentration in the procedural blanks was 0.18 ± 0.09 ng/mL, which was significantly lower than any concentration determined in digests of GSR tissue or in digests of larvae that had been feeding on GSR contaminated tissue.

TABLE 2—*Average concentration and relative standard deviation (RSD) of Sb, Ba, and Pb in wound and larvae digests (*n=*5).*

	Sb		Ba		Pb	
Digest	Average concentration (μg/g)	RSD (%)	Average concentration (μg/g)	RSD (%)	Average concentration (μg/g)	RSD (%)
Stab	0.04	6.0	0.16	1.5	0.14	1.0
Larvae	NQ*	NQ*	2.30	0.8	NQ*	NQ*
GSR (1)	0.35	1.2	0.91	0.4	1.00	0.3
GSR (2)	0.34	2.2	0.80	0.6	1.08	0.7

*NQ indicates "not quantified" due to levels below the determined limits of quantitations.

Outdoor Study—Late Summer

Concentrations of Sb, Ba, and Pb in larvae collected from the GSR tissue and control tissue during the late summer study are given in Fig. 3. The three elements were detected in larvae (species not identified) collected from GSR tissue on days 3 and 4 but the elements were not detected in larvae from the control (stabbed) tissue for the corresponding time points. For subsequent days, Sb was present at low levels in larvae from GSR tissue collected on days 9, 10, and 15 as well as larvae collected from the stabbed tissue on

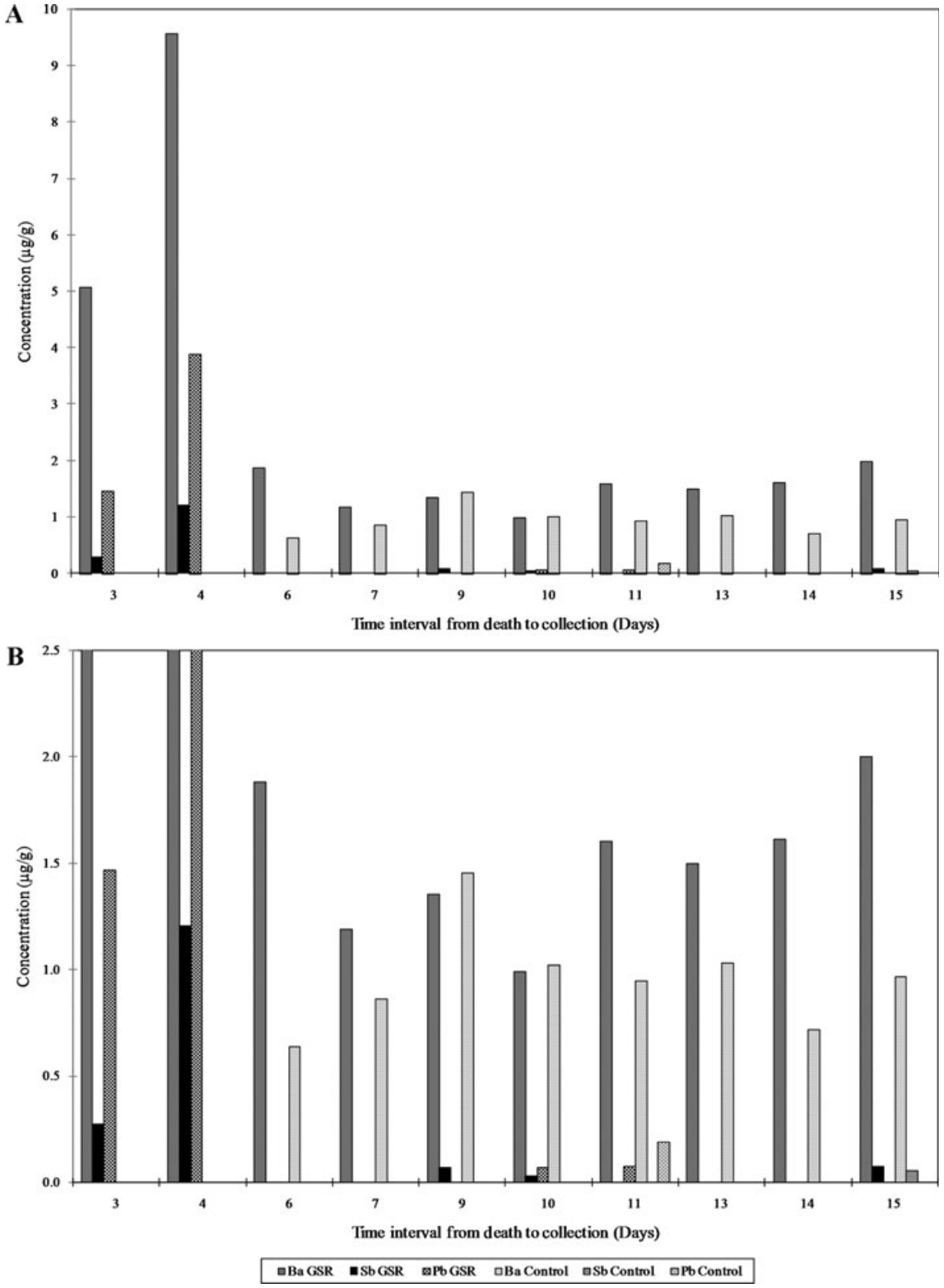

FIG. 3—*Concentration of Sb, Ba, and Pb in larvae collected during late summer study (A) full scale and (B) rescaled to show concentrations at later time points. "Gunshot residue" indicates larvae collected from GSR tissue while "Control" indicates larvae collected from stabbed tissue.*

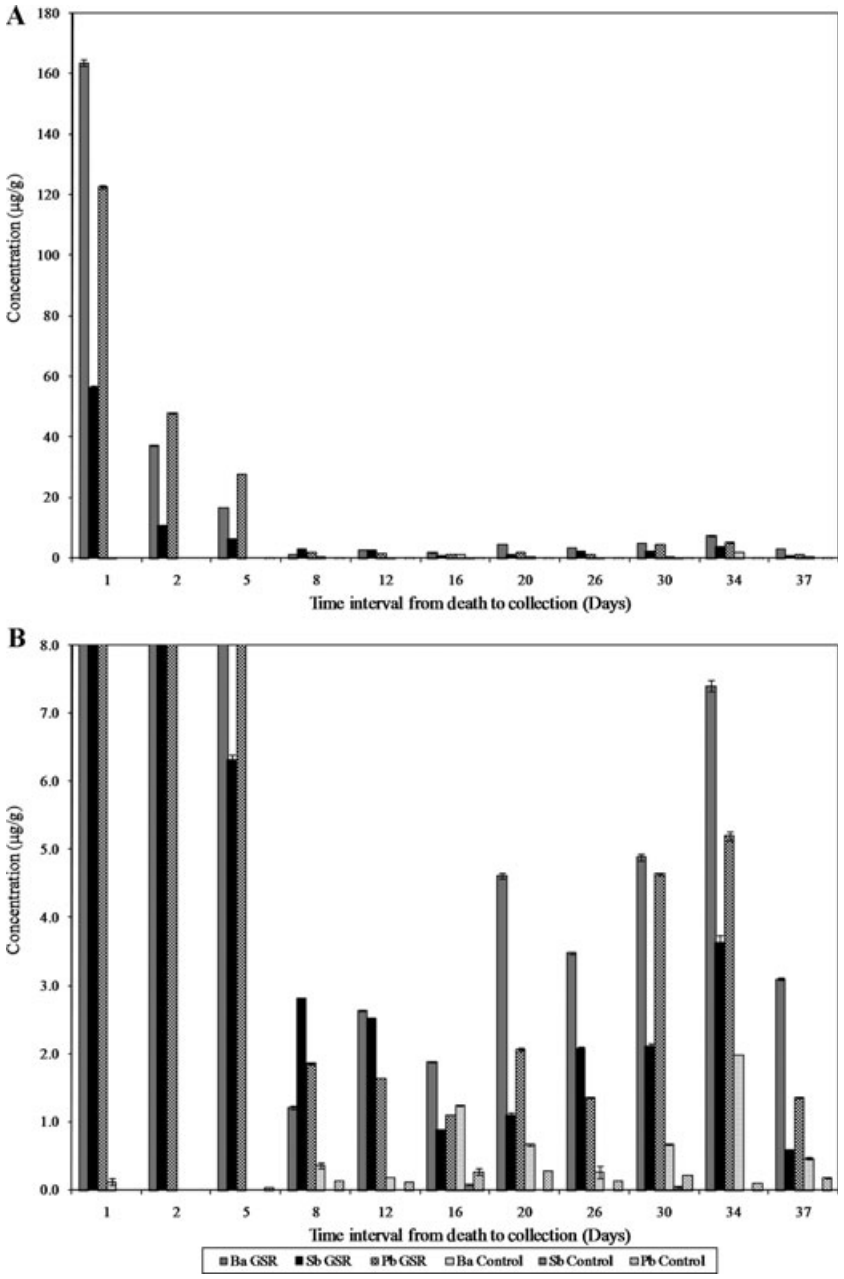

FIG. 4—*Concentration of Sb, Ba, and Pb in wounds collected during late summer study (A) full scale and (B) rescaled to show concentrations at later time points. ''Gunshot residue'' indicates GSR tissue while ''Control'' indicates stabbed tissue that was used as a control.*

day 15. Lead was present in GSR larvae only on days 10 and 11 as well as day 11 for larvae feeding on the stabbed tissue. Barium was present in all larvae at comparable levels irrespective of GSR or control tissue.

Variability in element concentrations determined on different days is likely because of the sample collection procedure. Larvae were more likely to be feeding on tissue within the wound tract rather than the skin surface where the majority of GSR was deposited. Higher element concentrations in larvae collected on earlier days are potentially due to larvae feeding closer to the surface. However, as time goes on and the surface becomes consumed, larvae feed deeper in the wound tract where there is less GSR.

During the late summer study, the 11 wounds in the GSR and control pigs were collected over a 37-day period, and the three elements characteristic of GSR were determined at all time points for GSR tissue samples (Fig. 4). For the control tissue, Sb was only observed on days 16 and 30 at concentrations of 0.08 µg/g tissue and 0.05 µg/g tissue, respectively. Barium was observed in the control wound digests for all time points with the exception of days 2 and 5 and concentrations ranged from 0.12 µg/g tissue (day 1) to 1.99 µg/g tissue (day 34). Lead was observed in the control wound digests for all time points with the exception of days 1 and 2 and concentrations ranged from 0.04 µg/g tissue (day 5) to 0.28 µg/g tissue (day 20).

Antimony concentrations in the GSR tissue ranged from 56.5 µg/g tissue (day 1) to 0.59 µg/g tissue (day 37). Barium concentrations ranged from 164 µg/g tissue (day 1) to 1.21 µg/g tissue (day 8) while lead concentrations ranged from 123 µg/g tissue (day 1) to 1.09 µg/g tissue (day 16). With the exception of Ba concentration in control tissue from day 34, concentrations of Sb,

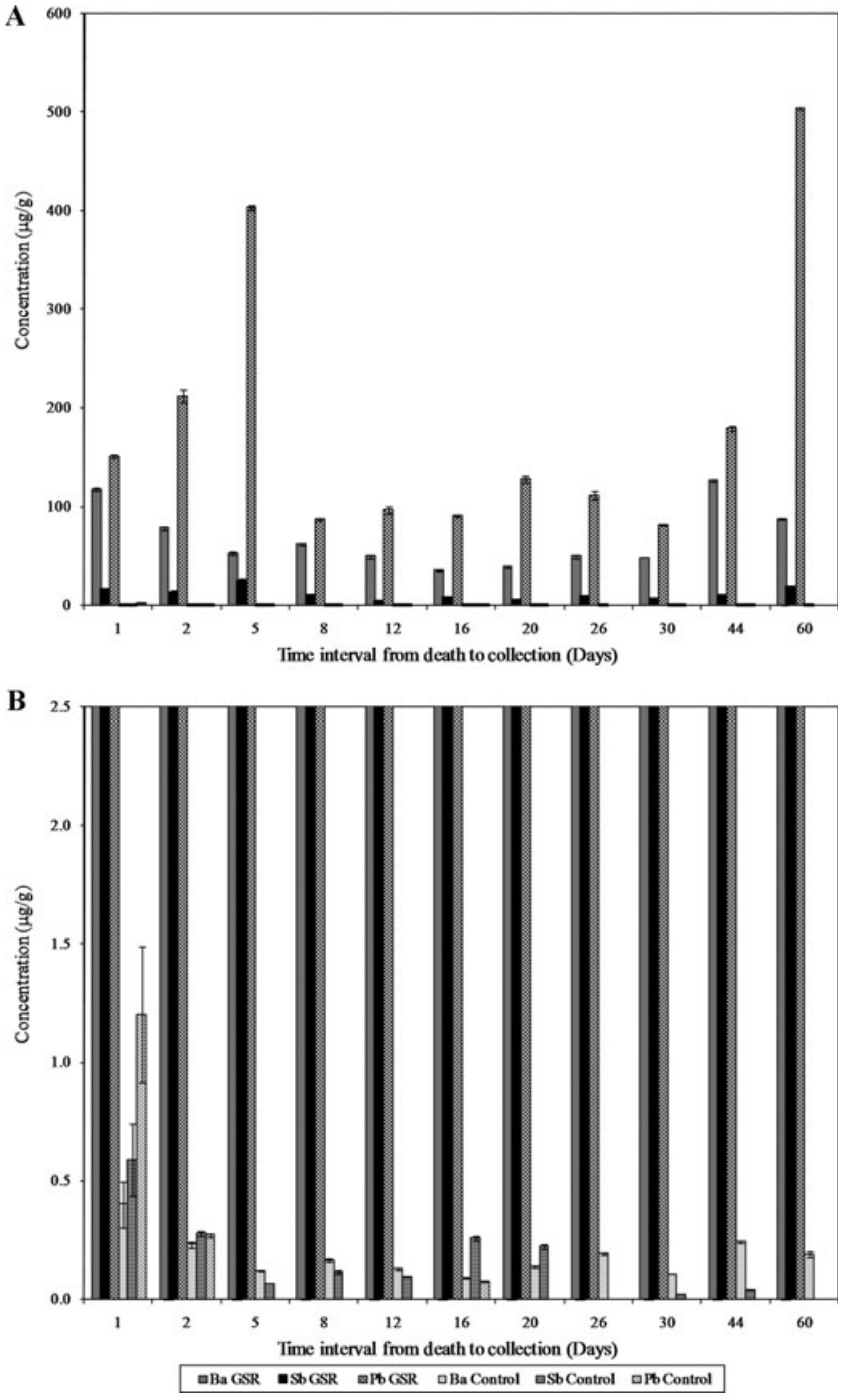

FIG. 5—*Concentration of Sb, Ba, and Pb in wounds collected during winter study (A) full scale and (B) rescaled to show concentrations at later time points. "Gunshot residue" indicates GSR tissue while "Control" indicates stabbed tissue that was used as a control.*

Ba, and Pb in the GSR tissue were approximately one order of magnitude greater than in the control tissue. Although the difference in Ba concentration between the control and GSR tissue on day 34 may not be significant, the differences in Sb and Pb indicate that there is still a significant difference between the GSR components in the GSR digest versus the control digest.

The decrease in Sb, Ba, and Pb in GSR tissue after day 1 is likely due to a partial loss of surface GSR. Significant rainfall occurred between the collection time on days 1 and 2, likely washing off surface GSR. Between days 2 and 5, remaining surface GSR was likely lost due to wind and decompositional fluid seepage. Additional rainfall occurred on the evening of the fifth day. Because of wind, rain, skin slippage, and active decay processes, it can be assumed that only the GSR that had tattooed into the skin remained by day 8, accounting for the apparent leveling off that was observed for GSR component levels in the tissue (Fig. 4). Nonetheless, GSR was detected at significant levels through the full 37-day sampling period, through all stages of decomposition.

The day-to-day variations in element concentrations in the GSR tissue are at least partially influenced by the sample collection procedure. Samples for digestion were cut approximately 1 cm from the bullet entrance wound. However, the distribution of GSR

around the entrance was not uniform, leading to differences in concentration of the elements present. Quantification of element concentrations was not a goal of this research as GSR determination is mainly based on a qualitative identification of the elements of interest.

Outdoor Study—Winter

During the winter study, decomposition did not advance to the same stage as in the late summer. By day 60, bloating was not evident although signs of putrefaction were apparent. The three elements were detected in both the control and GSR tissue digests for all time points (Fig. 5). Antimony was detected in all control tissues, with the exception of days 26 and 60; however, antimony concentrations were all <0.60 μg/g tissue. Barium was also present at all time points in the control tissue, with concentrations <0.50 μg/g tissue. Lead was detected in the control tissue on days 1, 2, and 16 at concentrations of 1.20, 0.27, and 0.07 μg/g tissue, respectively.

In the GSR tissue digests, Sb concentrations ranged from 35.6 μg/g tissue (day 5) to 5.23 μg/g tissue (day 12). Barium concentrations ranged from 126 μg/g tissue (day 44) to 34.9 μg/g tissue (day 16) while Pb concentrations ranged from approximately 500 μg/g tissue (day 60, beyond linear calibration range) to 81.3 μg/g tissue (day 30). As previously observed in the late summer study, concentrations of Sb, Ba, and Pb in the GSR tissue were one to two orders of magnitude greater than in the control tissue digests, and GSR elements were detected throughout the full sampling period (60 days).

Element concentrations were less variable in the winter study than in the late summer study, which is likely due to the lack of decomposition and insect activity. During late summer, decomposition had progressed to the desiccation stage by day 37. In the winter study, temperatures were sufficiently cold that decomposition was inhibited; by day 60, decomposition was not evident. Determination of GSR in the tissue samples was more dependent on the decomposition stage rather than the time since the wound was inflicted. With digestion of wound tissue and subsequent ICP-MS analysis, the three characteristic GSR elements were detected at significant levels in both the summer and winter studies through the full sampling period.

Conclusions

Although SEM/EDS is currently the method of choice for GSR detection, ICP-MS can play a role in the chemical identification of GSR in tissue as well as blowfly larvae. Using this technique, GSR was detected through advanced stages of decomposition and was not adversely affected by environmental conditions. Additionally, it has been shown that concentrations of GSR components in tissue depend more on the stage of decomposition rather than the amount of time between death and analysis.

These results, along with the similarities between porcine and human tissue, indicate that ICP-MS of tissue digests could provide a chemical means of identifying gunshot wounds in human victims. Unlike SEM/EDS, which proved unreliable beyond 1 day after death, the ability to detect GSR components by ICP-MS was not hindered by environmental factors. ICP-MS of tissue digests may be useful to a pathologist in the identification of suspected gunshot wounds when decomposition and larval activity have precluded conventional means of wound identification.

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