Shigetoshi Kage,[1] Ph.D.; Keiko Kudo,[2] Ph.D.; Akiharu Kaizoji,[1] B.S.; Jun-ichi Ryumoto,[1] B.S.; Hideaki Ikeda,[1,2] B.S.; and Noriaki Ikeda,[2] M.D.

A Simple Method for Detection of Gunshot Residue Particles from Hands, Hair, Face, and Clothing Using Scanning Electron Microscopy/Wavelength Dispersive X-Ray (SEM/WDX)

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ABSTRACT: We devised a simple and rapid method for detection of gunshot residue (GSR) particles, using scanning electron microscopy/wavelength dispersive X-ray (SEM/WDX) analysis. Experiments were done on samples containing GSR particles obtained from hands, hair, face, and clothing, using double-sided adhesive coated aluminum stubs (tape-lift method). SEM/WDX analyses for GSR were carried out in three steps; the first step was map analysis for barium (Ba) to search for GSR particles from lead styphnate primed ammunition, or tin (Sn) to search for GSR particles from mercury fulminate primed ammunition. The second step was determination of the location of GSR particles by X-ray imaging of Ba or Sn at a magnification of ×1000–2000 in the SEM, using data of map analysis, and the third step was identification of GSR particles, using WDX spectrometers. Analysis of samples from each primer of a stub took about 3 h. Practical applications were shown for utility of this method.

KEYWORDS: forensic science, gunshot residue, scanning electron microscopy/wavelength dispersive X-ray analysis

Gunshot residue (GSR) has been used in criminalistics to determine whether or not a person had discharged a firearm. GSR particles are produced from the primer, propellant, metals contained in the bullet, bullet jacket, cartridge case, and gun barrel when a gun is fired. Among them, GSR particles derived from the primer are specific to residues produced by the discharge of a gun. Most ammunition contains lead styphnate or mercury fulminate as the basic primary explosive ingredient. Combinations of the elements, lead (Pb), barium (Ba), and antimony (Sb) have been found in GSR particles based on lead styphnate primers (1). GSR particles based on mercury fulminate primers contain little mercury (Hg). Tin (Sn) and antimony (Sb) are the most commonly found elements (2). The origin of Sn in the GSR particle is not the primer mixture, which mainly consists of mercury fulminate, potassium chlorate, and antimony sulfide, but rather a foil disc made of Sn (2).

Automated search systems for GSR particles have been developed, using scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) spectrometer (3–5), and are commonly used in the countries where shootings are frequent. Although these systems are simple and useful, they are not always available in the countries where shootings are not so frequent.

We devised a simple, rapid method to detect GSR particles, using a scanning electron microscopy/wavelength dispersive X-ray (SEM/WDX) spectrometer, equipment generally used to analyze inorganic elements.

Experimental Procedure

A JEOL JXA-8800 electron microprobe (Tokyo, Japan) was used for GSR particle analysis. The instrument is equipped with two WDX spectrometers, using lithium fluoride (LiF) and pentaerythritol (PET) crystals, a motorized stage drive, and a nine-sample holder. The test firings were carried out in an indoor shooting range by playing 0.38 Smith & Wesson special ammunition, using a 0.38-caliber revolver, and 7.62 mm Russian Tokarev ammunition, using a semiautomatic pistol. The samples were collected immediately after the firing by the tape-lift method, using 10 mm-diameter aluminum stubs coated with double-side adhesive tape (NW-10SF, Nichiban Co., Tokyo, Japan) from both hands, face, and hair, and with double-side adhesive carbon tape (Nisshin EM Co., LTD, Tokyo, Japan) from clothing. The surface of hand or face was dabbed by the tape 50 times, and that of hair or clothing 200 times (6,7). The stubs were thickly (dark brown) coated with carbon by a carbon coater (SC-701C, Sanyu Denshi Co., LTD, Tokyo, Japan) prior to examination, in order to reduce electron charging of the sample.

GSR Particle Analysis

SEM/WDX analyses for GSR were carried out in three steps. The first step was automatic map analysis of Ba to search for GSR particles from lead styphnate primed ammunition, or Sn for

[1] Forensic chemist, technical examiner, technical examiner, and forensic chemist, respectively, Forensic Science Laboratory, Fukuoka Prefectural Police Headquarters, 7-7, Higashikoen, Hakata-ku, Fukuoka 812-8576, Japan.

[2] Lecturer, guest researcher, and professor, respectively, Department of Forensic Pathology and Sciences, Graduate School of Medical Sciences, Kyushu University, 3-1-1, Maidashi, Higashi-ku, Fukuoka 812-8582, Japan.

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GSR particles from mercury fulminate primed ammunition. The element, Ba or Sn, was selected for giving most high intensity in the main element of GSR particles, respectively. Map analysis was done by measuring Ba $L\alpha_1$ or Sn $L\alpha_1$ X-ray, using PET crystal at the dwell time of 10 ms and the pixel size of 10 μm. The electron beam was not scanned ("point mode") in order to obtain the constant sensitivity without being influenced by magnification. An automatic search in half of the stub area, 6×6 mm^2, was done. The search time for one element was 1.3 h. The second step was determination of the location of GSR particles by X-ray imaging of Ba or Sn at a magnification of ×1000–2000 in the SEM after semiautomatically moving the sample stage close to a point of Ba $L\alpha_1$ or Sn $L\alpha_1$, using the data from the map analysis. The third step was identification of GSR particles by their spectra generated from these WDX spectrometers. Analysis time of one crystal of a GSR particle was 3 min. The electron beam was scanned in a square of a side equal to the particle diameter positioned about the center of the particle ("raster mode"). Accelerating voltage and beam current were set under 20 keV and 30 nA, respectively.

Results and Discussion

All samples collected from hands, face, hair, and clothing after firing the ammunition based on lead styphnate primer or mercury fulminate primer showed positive results of GSR in this experiment. The advantages of using SEM/WDX are a superior energy resolution and elemental sensitivity. The drawbacks of SEM/WDX are high beam current and long analysis time, but there was no loss of particle due to those in this method.

The established method is a map analysis in the main element of GSR particles, Ba or Sn, to locate particles in the first step. Automated search systems by SEM/EDX (3–5) involved use of the backscattered electron (BSE) imaging to search for location of the GSR particles. The BSE signal increases with increase in the average atomic number (z). GSR particles will appear to be brighter dots than most environmental particles on the BSE image. The BSE signal from a particle was compared with a preset video threshold. If the BSE video threshold is set too high, GSR particles may be missed, and if it is set too low, many nonGSR particles can be detected. Map analysis of Ba or Sn using our method was more specific for GSR than the BSE imaging of an automated search system with EDX analysis.

There is another disadvantage which is the X-ray overlap of GSR components in an EDX spectrometer. Since most EDX spectrometers have an energy resolution of 140 to 160 eV, there are interferences for the Ba $L\alpha_1$ (4.47 keV, 2.78 Å) from titanium $K\alpha_1$ (4.51 keV, 2.75 Å), for the Sn $L\beta_1$ (3.66 keV, 3.39 Å) from the Sb $L\alpha_1$ (3.60 keV, 3.44 Å) and calcium $K\alpha_1$ (3.69 keV, 3.36 Å). Compared to the EDX spectrometer, WDX spectrometers have a superior energy resolution (10 eV) and elemental sensitivity. Figure 1 shows the typical map data of Ba $L\alpha_1$. Black points in the map

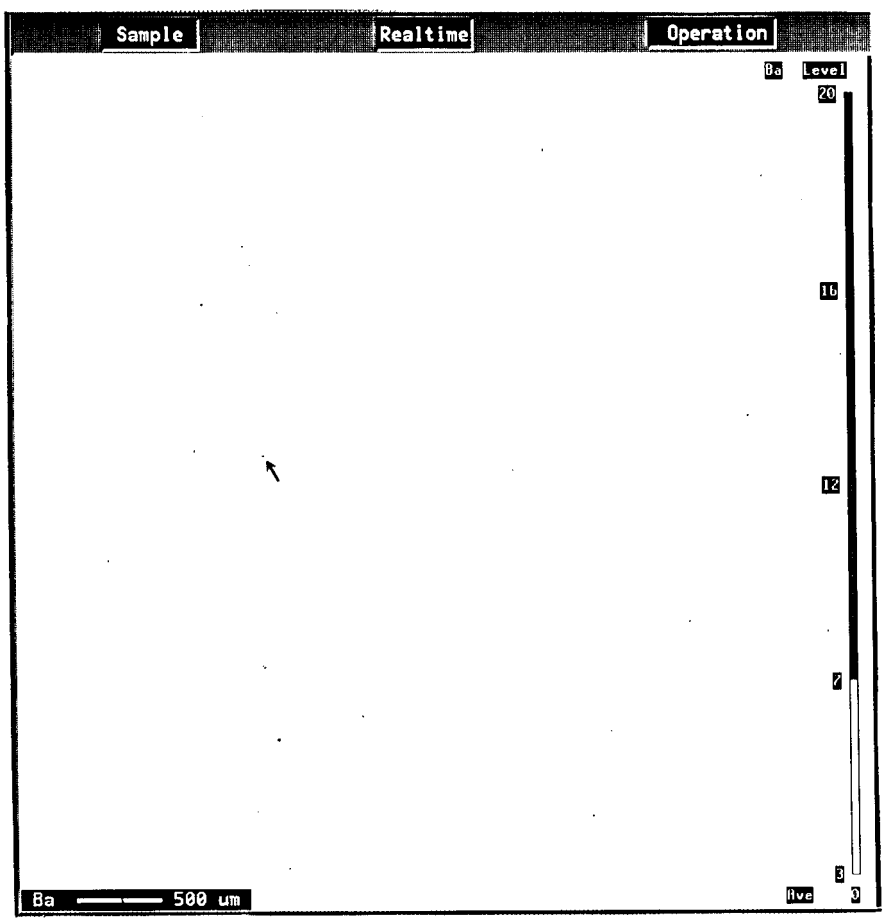

FIG. 1—*Map analysis data of Ba $L\alpha_1$ in samples from the shooter who fired ammunition based on lead styphnate primer.*

show positions of particles containing Ba. An arrow points to one of them. Points show the intensity of Ba and the size of the particles. The detection of GSR particles in map analysis was influenced by the intensity of Ba or Sn in particles, especially. The detection limit of particle size was about 0.5 μm in diameter when the level in the intensity map of Ba or Sn was set at about 3.

In the second step, location of GSR particles was determined by X-ray imaging of Ba or Sn at a magnification of ×1000–2000 in the SEM, a procedure which detects particles exceeding 0.5 μm in diameter. Using the data obtained from map analysis, SEM easily detected the GSR particles and their exact position by monitoring X-ray imaging of Ba for lead styphnate, or Sn for mercury fulminate. The X-ray imaging of Ba $L\alpha_1$ is shown in Fig. 2.

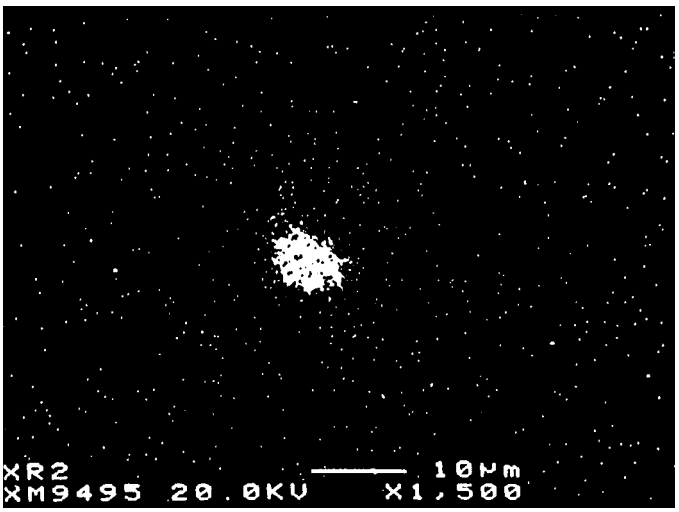

FIG. 2—*X-ray image of Ba $L\alpha_1$ of a typical GSR particle found in the sample from the shooter who fired ammunition based on lead styphnate primer (×1500).*

The third step was identification of GSR particles by WDX spectrometry. We could save time by analyzing GSR particles only when Sb was found in a particle by X-ray imaging at the second step. WDX spectra using two crystals (LiF, PET) in GSR particles of each type ammunition are shown in Figs. 3 and 4. In previous reports (3–5), Sulfur (S) was not easily identified in GSR particles because of a less than satisfactory energy resolution in the EDX spectrometer (140–60 eV). The spectrum of S $K\alpha_1$ (2.31 keV, 5.37 Å) was overlapped with that of Pb Mα (2.34 keV, 5.29 Å) in the EDX analysis. The spectrum of S $K\alpha_1$ in the WDX analysis could be distinguished from that of Pb Mα, as it has a superior energy resolution (10 eV) (8). Therefore, our method revealed Ba, Pb, Sb, and S in the GSR particles from ammunition based on lead styphnate primer. WDX analysis was found to provide a more accurate identification of GSR particles than EDX analysis.

In GSR particles from ammunition based on a mercury fulminate primer, Zeichner et al. (2) reported that Hg was not found in GSR particles collected from the shooter of Russian ammunition based on the mercury fulminate primer. They found only Sn and Sb. With our method, Sn, Sb, and S were identified and Hg was not found in GSR particles from the shooter. However, Hg was found in GSR particles from the cartridge case. This is explained by the fact that Hg would vaporize more easily from GSR particles moving with the burning propellant and hot gases than particles remaining in the cartridge case (2).

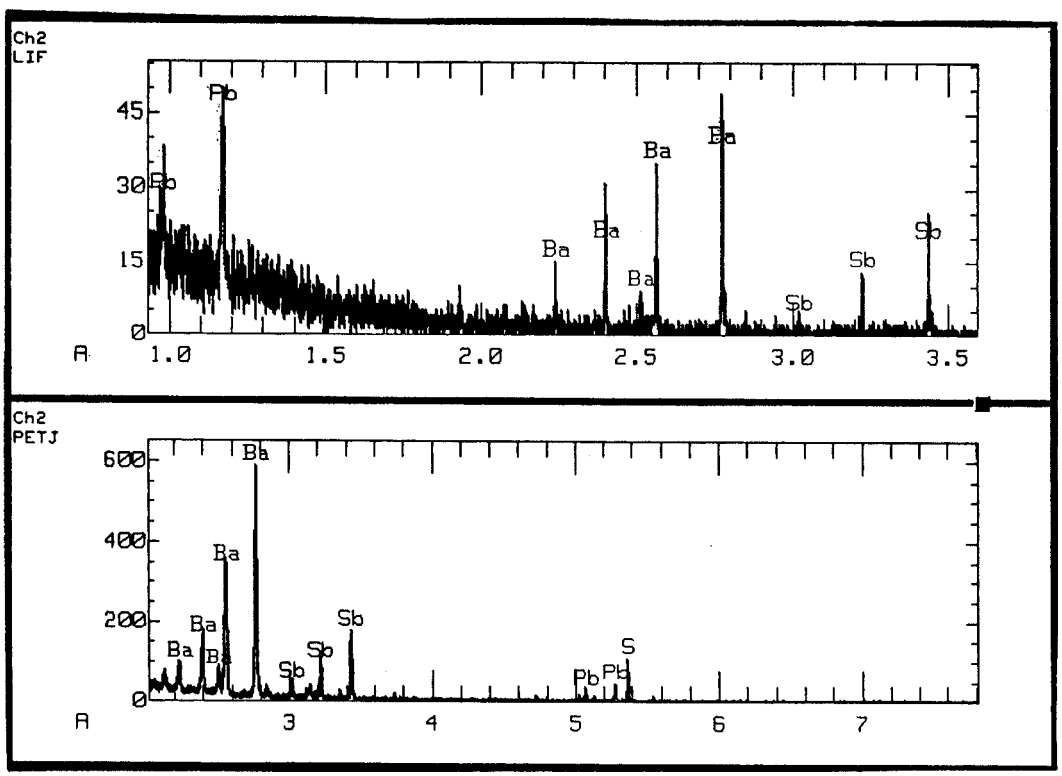

FIG. 3—*WDX spectra of a typical GSR particle found in the sample from the shooter who fired ammunition based on lead styphnate primer (top: LiF crystal, bottom: PET crystal).*

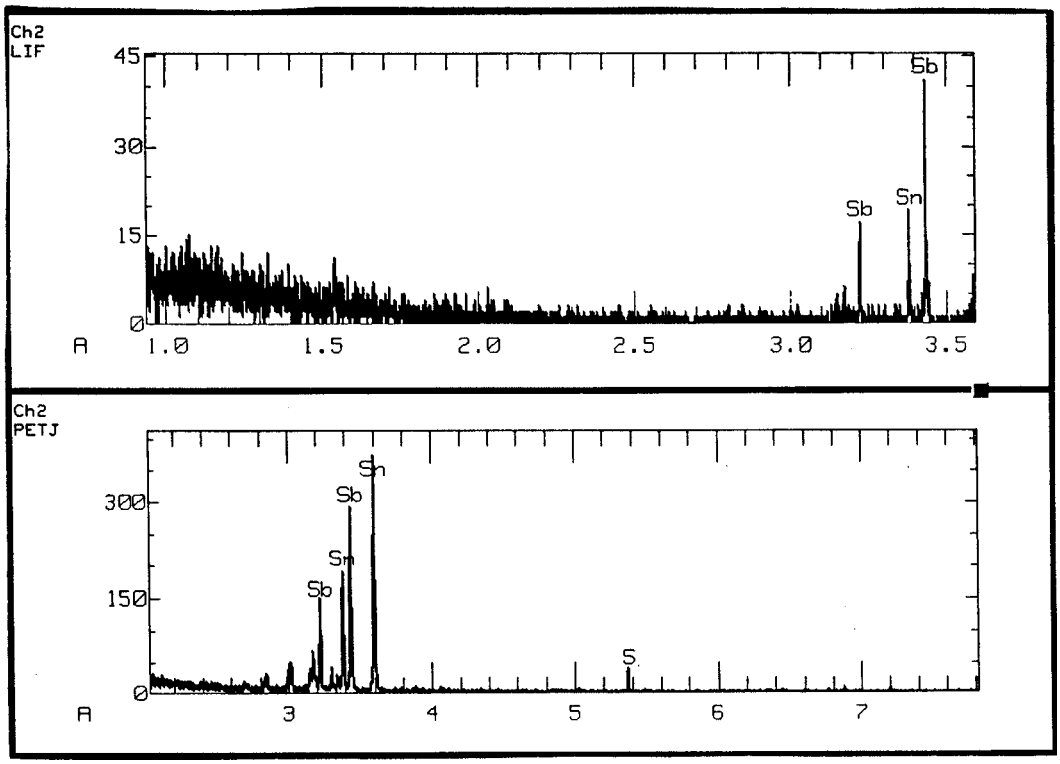

FIG. 4—*WDX spectra of a typical GSR particle found in the sample from the shooter who fired ammunition based on mercury fulminate primer. (top: LiF crystal, bottom: PET crystal).*

GSR particles deposited on a person are continuously lost as a result of normal activities. It is difficult to generalize as to the period over which the residues would be retained. It is known that the probability of finding particles on hands more than 3 h after firing is very low. However, a much longer persistence of GSR was found on hair and clothing (6). Various sampling methods (6,7,9,10) to collect extraneous materials from the sample and concentrate GSR particles onto a small area were developed. One of them, the tape-lift method (6,7), is a suitable technique due to its simple and fast collection of GSR particles from hands, face, hair, and clothing. Zeichner et al. (6) reported that 200 to 300 dabbings were necessary to achieve maximum collection efficiency from hair with the double-side adhesive, and 50 to 100 dabbings from hands. So were the repeated dabbings in our method. There was no loss of particles from the adhesive surface as a result of the repeated dabbings. However, electron charging was sometimes observed in samples from clothing. To reduce electron charging, we used double-side adhesive carbon tape instead of double-side adhesive tape.

Application

Case 1—Five burglars broke into the office of a forwarding agency. One burglar fired one round of 7.62 mm Russian Tokarev ammunition, using a semiautomatic pistol. He was captured by employees of the company at that time. The results of GSR analysis were positive on samples from a pair of leather gloves and a baseball cap the burglar used, but negative in samples from both of his hands and his hair.

Case 2—A gangster was arrested for having a Russian Tokarev semiautomatic pistol. It was suspected that he had fired five rounds of 7.62 mm Russian Tokarev ammunition, as a threat. The results of GSR analysis were positive in samples from a pair of cotton gloves and a balaclava seized 14 days after the firing of the weapon.

Case 3—A burglar who broke into a Chinese restaurant fired 0.38 Smith & Wesson special ammunition five times, using a 0.38-caliber revolver. He was arrested 10 h later and the samples were collected immediately. The results of GSR analysis were positive in samples from the right hand, face, and right cuff of a jersey, but negative in samples from the left hand and hair.

Case 4—A gangster in a car fired 19 rounds of 5.56 mm NATO ammunition into the office of the rival gang, using a M16 rifle. He was arrested 2 h later, and GSR samples were collected immediately. The results of GSR analysis were positive in samples from both hands, face, hair, and both cuffs of a suit.

Conclusion

A simple and rapid method for detection of GSR particles from hands, hair, face, and clothing of a shooter, using SEM/WDX, was established. Practical applications showed the utility of this approach. This method can be easily applied to various types of GSR, using automatic map analysis of the main element of GSR particles.

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Additional information and reprint requests:
Noriaki Ikeda, M.D.
Department of Forensic Pathology and Sciences
Graduate School of Medical Sciences
Kyushu University
3-1-1, Maidashi, Higashi-ku, Fukuoka 812-8582, Japan