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Evaluation of Instrumental Parameters for Automated Scanning Electron Microscopy/Gunshot Residue Particle Analysis

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ABSTRACT: Computer-controlled analytical scanning electron microscope (SEM) parameters such as the minimum particle size, video threshold, digital electron beam point spacing, video dwell time, X-ray counting time, and analysis mode, affect the time and accuracy of automated gunshot residue (GSR) particle analysis. The effects of these parameters on automated analysis of a GSR sample are described. This study was performed using custom-written software which includes several features, such as simultaneous energy and wavelength-dispersive X-ray analysis, that are not available in commercial packages.

Proper setting of the backscattered electron (BSE) video threshold is critical for automated SEM/GSR particle analysis. Use of a calibrated BSE detector facilitates reproducible setting of the BSE video threshold.

With the results from this and similar studies using different GSR samples, it should be possible to develop standard procedures for automated SEM/GSR particle analysis.

KEYWORDS: forensic science, gunshot residue, microscopy, computers

Gunshot residue (GSR) particles are produced when a gun is fired. These particles are of many different types, most of which contain some combination of the elements lead, antimony, and barium. An individual GSR particle, by definition, contains at least the chemical elements lead, antimony, and barium. Identification of individual GSR particles is done using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) spectrometer [*1*]. An analyst manually scans the sample while viewing the backscattered electron (BSE) image. GSR particles will appear brighter in the BSE image than either the substrate (usually an adhesive surface) or most environmental particles. Potential GSR particles are analyzed using the EDX spectrometer, with which the EDX spectrum is examined for the presence of lead, antimony, and barium. The likelihood of finding GSR particles depends upon several factors, including the type of gun and ammunition fired, the type of surface sampled (hand, clothing, furniture, or other surface), the sampling medium, the time after firing, and the activity level of the surface being sampled.

Using a computer-controlled SEM it is possible to perform unattended GSR particle searching, location, and identification. The use of commercially available automated SEM

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systems for GSR particle analysis has been reported [2–4]. Each system uses BSE imaging for locating GSR particles and EDX analysis for GSR particle identification. However, there are several instrumental parameters, for example, the BSE video threshold, that need to be considered for automated GSR particle analysis that are not relevant to manual GSR particle analysis. Previous studies have not considered the effect of these parameters on automated GSR particle analysis. Also, there are significant differences in the instrumental parameters used in earlier studies. For example, Tillman [2] uses a magnification of ×501 and searches for particles larger than 2 μm in diameter, whereas White and Owens [3] use a magnification of ×1800 and search for particles greater than 0.5 μm in diameter. The magnification and minimum particle size affect the automated GSR particle analysis time. For example, for an automated SEM system, a decrease in the minimum particle size from 2 to 0.5 μm increases the analysis time by at least a factor of 16.

The purpose of the work reported here is to determine the effect of critical instrumental parameters on automated SEM/GSR particle analysis. Automated GSR particle data were obtained using different minimum particle sizes, BSE video thresholds, digital electron-beam point spacings and dwell times, and X-ray counting times and analysis modes. The data were obtained using custom-written software specifically designed for automated SEM/GSR particle analysis. An important feature of the software used in this study is its ability to do EDX and wavelength-dispersive X-ray (WDX) analysis simultaneously. The superior energy resolution and elemental sensitivity of WDX analysis provides better GSR particle identification than EDX analysis.

Automated SEM/GSR analysis can be faster and, in the long run, less costly than manual analysis. However, another important advantage is that it should be possible to standardize the SEM/GSR analysis procedure. A standardized procedure would be extremely useful for interlaboratory comparison of automated SEM/GSR results and aid in developing improved GSR particle sampling methods. The results of this study should provide an initial framework for the development of a standardized automated SEM/GSR procedure.

Experimental

A JEOL JXA-8600 electron microprobe (JEOL USA, Peabody, Massachusetts) was used for automated GSR particle analysis. The instrument is equipped with a solid-state BSE detector, EDX analysis system (TN-5500, Tracor Northern, Madison, Wisconsin), digital electron beam control, and Tracor Northern (TN-5600) WDX analysis and sample stage automation package. There are five WDX spectrometers, three of which can be configured for automated GSR particle analysis. The software, a modified version of Tracor Northern's particle recognition and characterization (PRC) [2] program, incorporates several features not available in the PRC program, including BSE video threshold calibration, 20-sample sequential analysis, and WDX analysis. Data analysis was done using the EXPLOR computer program [5]. EXPLOR is a package of computer programs designed for automated particle analysis data handling, reduction, and statistical analysis. The programs are written in Fortran-77 and run on a Digital Equipment Corp. Microvax II minicomputer.

Only one GSR sample was used for this study. The sample was collected immediately after firing one bullet from a .38 caliber revolver. The sample was collected using a 12.5-mm-diameter aluminum pin-type SEM sample stub covered with double-sided sticky tape. The stub was repeatedly dabbed on the thumb/web/forefinger area of the hand until the adhesive was no longer tacky. The sample was coated with a thin carbon film prior to analysis.

Automated GSR Particle Analysis

WDX Analysis

Automated SEM particle analysis systems use EDX spectrometers for elemental analysis. Most EDX spectrometers have an energy resolution of 140 to 160 eV (for manganese K_α radiation); consequently there can be severe X-ray overlap in the EDX spectrum. For example, for the three lead X-ray peaks found in a 0 to 20-keV EDX spectrum, only the least intense $L_{\beta 1}$ (12.61 keV) line has no common interference. The lead M_α X-ray (2.34 keV) line is interfered with by the sulfur K_α (2.31 keV) and molybdenum L_α (2.29 keV) lines, and the lead $L_{\alpha 1}$ (10.55 keV) line is interfered with by arsenic K_α (10.53 keV). There are also common interferences for barium L_α (4.47 keV) from titanium K_α (4.51 keV) and for antimony L_α (3.60 keV) from calcium K_α (3.69 keV) and tin $L_{\beta 1}$ (3.66 keV). Because of the better energy resolution (~10 eV) and elemental sensitivity of WDX spectrometry, it should provide superior GSR particle analyses. The automated SEM/GSR program used in this study can perform WDX and EDX analysis simultaneously. Three different WDX spectrometers are used to measure lead M_α, antimony L_α, and barium L_α X-rays using pentaerythritol (PET) crystals. There should be no significant interferences when using WDX spectrometry for GSR particle analysis. Comparison of EDX and WDX spectra from a GSR particle is shown in Fig. 1.

BSE Video Threshold

The BSE intensity emitted when a primary electron beam strikes a sample is a function of the average atomic number (z) of the sample. The BSE signal increases with increasing z. For an average z, the BSE intensity decreases with decreasing particle thickness. In automated GSR particle analysis, the BSE signal from a particle is compared with a preset video threshold. If the signal exceeds the threshold, then the particle is sized and analyzed. Setting the BSE video threshold can be very difficult. If the threshold is set

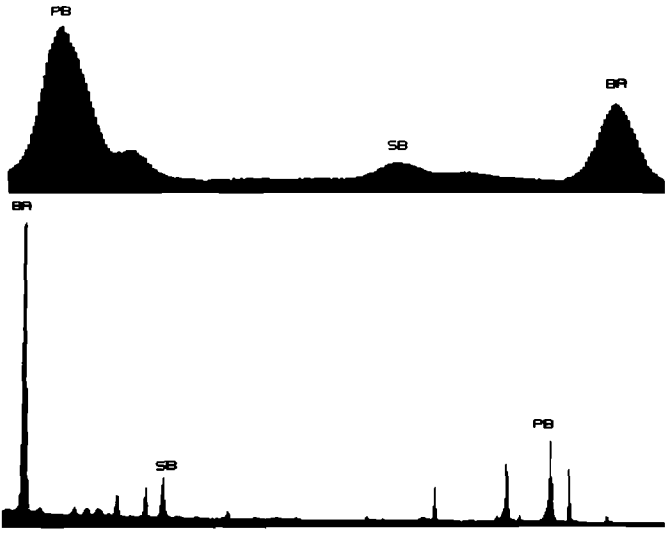

FIG. 1—*Portion of EDX spectrum from a GSR particle showing Pb-M, Sb-L, and Ba-L X-ray lines* (top). *WDX spectrum of a GSR particle having the same energy range as the EDX spectrum but from high to low energy* (bottom).

too high, then GSR particles may be missed; if set too low, then too many non-GSR particles will be analyzed, thus increasing the analysis time. The author has calibrated the BSE detector before automated GSR particle analysis, which made it very easy to set the video threshold reproducibly. Figure 2 is the BSE calibration curve for the detector used in this study. The calibration curve is determined by measuring the BSE signal from several thick, flat elemental standards.

Sample Analysis

It is possible to analyze twenty 12.5-mm-diameter GSR samples sequentially. The operator enters the starting coordinates for each sample before the analysis begins. Also, the number of fields of view in the X and Y directions are entered, along with the distance between the fields of view. Particles are located by digitally scanning the electron beam across the field of view. At each point in the scan, the BSE signal is averaged for a preset dwell time and compared with the video threshold. If the BSE signal exceeds the threshold, then the beam is scanned across the particle until the signal drops below the threshold. The beam is repositioned to the center of this X chord and scanned in the Y direction until the BSE signal drops below the threshold. This process is iterated to locate the particle center. Eight diameters are measured through the particle center to determine the size, shape, area, and perimeter. The electron beam can either be positioned at a point at the center of the particle ("point" mode) or rastered over the particle surface ("raster" mode) during X-ray acquisition. If rastered, the electron beam is scanned in a square of a side equal to the average particle diameter positioned about the center of the particle. EDX and WDX data are obtained simultaneously from the particle. After EDX data acquisition, the WDX spectrometers are moved to a background position and counted for a preset time. An X-ray region-of-interest (ROI) analysis is performed on the EDX spectrum for up to 31 elements. An X-ray peak is considered to be present in an ROI if the net X-ray counts above a straight line background exceed three times the square root of the background counts in the ROI. The same criterion is used to determine if a peak is detected by the WDX spectrometers. The size, shape, and X-ray data are stored in a disk, along with the field number and the particle coordinates within the field. The program can be configured to store the entire EDX spectrum for some or all particles for subsequent examination based on the results of the EDX/WDX analyses. Spectra can be stored for particles that contain *only* specific elements or for particles that contain *at least* the elements specified. For example, EDX spectra would be stored for particles in which lead, antimony, and barium are found by WDX spectrometry. Once the particles

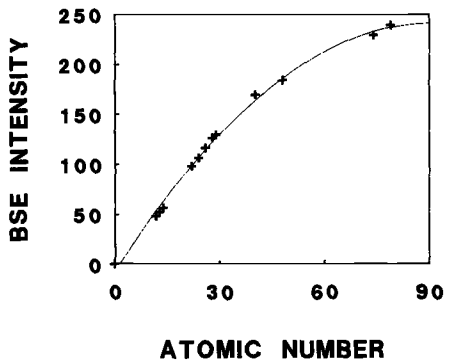

FIG. 2—*Calibration curve of the BSE intensity versus the atomic number.*

in a field of view have been analyzed, then the sample stage is moved to the next field of view. This process is repeated until all fields have been analyzed or the analysis is stopped. The program can be configured to stop the analysis once a preselected number of particles have been analyzed or a preselected number of particles with a specific elemental composition have been found. For example, the analysis might be stopped once a given number of particles containing lead, antimony, and barium have been found by WDX spectrometry.

After a sample has been analyzed, then the stage is moved to the starting field of the next sample. Once all samples have been analyzed, the data set or sets are transferred to the EXPLOR program for analysis.

The data are scanned to locate those particles in which lead, antimony, and barium have been detected by EDX or WDX spectrometry. The particles can be relocated in the electron microprobe for further X-ray analysis or photomicrography.

Results

The author performed five automated SEM/GSR experiments. The instrumental conditions used in the experiments are given in Table 1.

BSE Video Threshold Experiment

Automated analyses were done using BSE video thresholds of 50, 75, 100, 125, and 150 based on a digitized BSE video signal gray level of 0 to 255. The same area of the sample was repeatedly analyzed for particles >0.5 μm in diameter. Data were obtained for 400 particles at each threshold setting. Table 2 summarizes the results of the threshold experiment.

At a threshold of 50 there were 303 GSR particles, of which 66 (22%) contained a lead-antimony-barium element combination (Pb-Sb-Ba) (determined by WDX spectrometry). The non-GSR particles contained the element combinations potassium-chlorine, barium-sulfur, iron, calcium, aluminum-silicon, and copper-zinc. At a threshold of 100 there were 367 GSR particles, of which 139 (38%) contained Pb-Sb-Ba. The remaining non-GSR particles contained the element combinations iron, barium-sulfur, and copper-zinc. At a threshold of 150 there were 383 GSR particles, of which 148 (39%) contained Pb-Sb-Ba. The remaining non-GSR particles contained barium-sulfur. Obviously, as the BSE threshold increased, the percentage of non-GSR particles decreased. The majority of non-GSR particles had a lower average z than the GSR particles. For example, most mineral particles have a BSE signal of <75, whereas most iron-based metals have a BSE signal <115. It can also be seen in Table 2 that the relative percentage of each GSR

TABLE 1—*Instrumental conditions used for the automated SEM/GSR experiments.*[a]

	Threshold	Dwell Time	Point Spacing	X-Ray Mode	X-Ray Time
Magnification, ×	600	600	300	300	300
Minimum size, μm	0.5	0.5	1.0	1.0	1.0
Threshold	variable	100	100	100	100
Dwell time, μs	4	variable	4	4	4
Interpoint spacing, μm	0.25	0.25	variable	0.5	0.5
X-ray analysis mode	raster	raster	raster	variable	raster
X-ray count time, s	9 (3)[b]	9 (3)	9 (3)	9 (3)	variable

[a]Accelerating voltage = 30 keV; beam current = 10 nA; X-ray takeoff angle = 40°; EDX energy range = 0–20 keV; and sample working distance = 11 mm.

[b]The WDX background count time is in parentheses.

TABLE 2—*Summary of results from the BSE video threshold experiment.*[a]

	Threshold				
	50	75	100	125	150
Fields	49	139	230	341	754
Particle type					
Pb-Sb	98 (32)[b]	155 (47)	134 (36)	198 (53)	191 (50)
Pb-only	72 (24)	48 (15)	33 (9)	27 (7)	22 (6)
Pb-Sb-Ba					
EDX analysis	13	29	82	73	115
WDX analysis	66 (22)	79 (24)	139 (38)	122 (33)	148 (39)
Sb-only	34 (11)	26 (8)	3 (1)	1 (<1)	0 (0)
Pb-Ba	25 (8)	10 (3)	4 (1)	3 (1)	1 (<1)
Sb-Ba	8 (3)	10 (3)	54 (15)	23 (6)	21 (5)
Total	303	328	367	374	383
Pb-Sb-Ba particles per field[c]	1.34	0.57	0.60	0.36	0.20

[a]The data obtained are for 400 particles at each threshold setting.
[b]The percentage of total GSR particles is in parentheses.
[c]Based on WDX data only.

particle type varies with the video threshold. The relative percentage of Pb-only, Sb-only, and Pb-Ba particles decreases with increasing video threshold. However, the relative percentage of Pb-Sb-Ba, Pb-Sb, and Sb-Ba particles increases with increasing video threshold. Figure 3 contains the particle size distributions, at a threshold of 50, for the Pb-Sb (Fig. 3*a*), Pb-only (3*b*), Sb-only (3*c*), and Pb-Ba (3*d*) particle types. The Pb-only and Pb-Ba particles are predominantly submicrometre in size. The majority of Pb-Sb and Sb-only particles are greater than 1 μm in diameter. The decrease in the percentage of Pb-only and Pb-Ba particles with increasing video signal is due to the fact that the BSE signal from the submicrometre particles does not exceed the higher video thresholds. Even though most Sb-only particles are larger than 1 μm, the relative percentage of this particle type also decreases with increasing video threshold. This may indicate that the Sb-only particles have a platelet morphology. Large thin particles will emit a BSE signal that is comparable to those of smaller euhedral-shaped particles. Consequently, the BSE signal from the Sb-only particles does not exceed the higher video thresholds. Consequently, the GSR composition is enriched in the Pb-Sb-Ba, Pb-Sb, and Sb-Ba particle types at the higher video thresholds.

It was determined by Wolten et al. [*1*] that, of the particle types listed in Table 2, only Pb-Sb-Ba and Sb-Ba are characteristic of GSR. The other particle types are consistent but not unique to GSR. Because the Sb-Ba particle type comprises at most 15% of the total GSR particles (Table 2, threshold = 100), the remainder of the discussion will concern the detection of Pb-Sb-Ba particles only.

Though the percentage of Pb-Sb-Ba particles increases with increasing video threshold, the number of these particles per field decreases (Table 2). It is interesting to note that the number of Pb-Sb-Ba particles detected per field does not decrease when the threshold is increased from 75 (0.57 particles per field) to 100 (0.6 particles per field). To understand this discrepancy, the author examined the elemental compositions of the Pb-Sb-Ba particles for each BSE video threshold. Figure 4 contains ternary diagrams for the Pb-Sb-Ba particles found using video thresholds of 75 and 100. Ternary diagrams are plots of the relative intensity (RI) for Pb, Sb, and Ba from WDX analysis count rate data. The relative intensity is determined by dividing the WDX count rate for each element by the

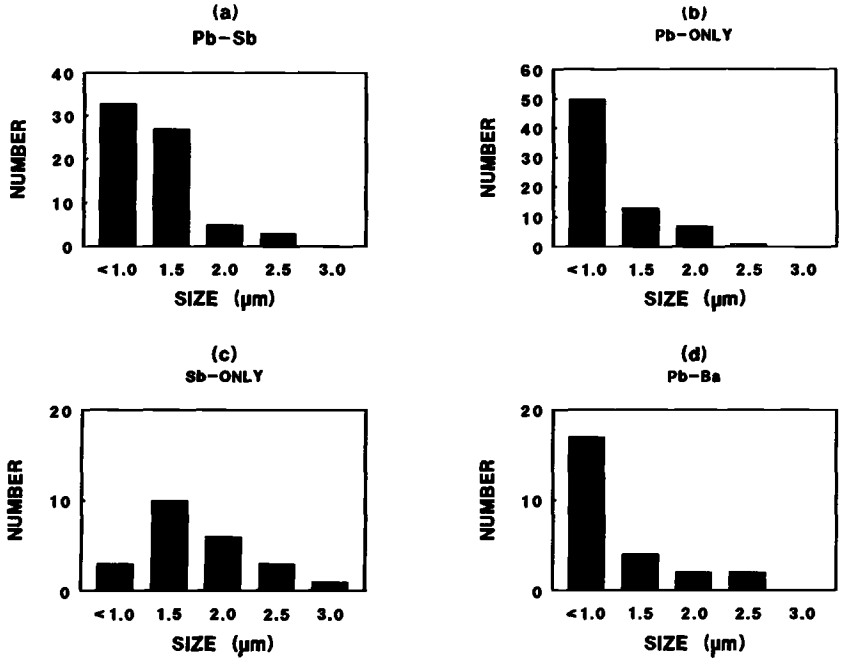

FIG. 3—*Particle size distributions for GSR particle types* (a) *Pb-Sb*, (b) *Pb-only*, (c) *Sb-only, and* (d) *Pb-Ba*.

total count rate for all three elements. The data have not been quantified using standards nor have they been corrected for matrix (ZAF) or particle size and shape effects. The ternary diagrams show that, at a video threshold of 100, the composition of the Pb-Sb-Ba particles changes from predominantly Pb-rich to both Pb-rich and Sb-rich particles (notc the concentration of data points near the Sb vertex in Fig. 4). There is a difference in the size distributions of the Pb-rich and Sb-rich Pb-Sb-Ba particles (Fig. 5). The average Pb-rich and Sb-rich particle sizes arc 1.7 and 3.1 μm, respectively. Almost 50% of the Pb-rich particles are less than 1 μm in diameter, whereas only 25% of the Sb-rich particles are submicrometre in size. These results indicate that there are two types of Pb-Sb-Ba particles. One type consists of small Pb-rich particles, which may originate primarily from the bullet. The other type consists of larger Sb-rich particles, which may originate from the primer.

The number of Pb-Sb-Ba particles found by WDX analysis is always greater than that for EDX analysis. The ratio of Pb-Sb-Ba particles detected using WDX versus EDX spectrometry decreases from 5.1 at a threshold of 50 to 1.3 at a threshold of 150.

BSE Video Signal Dwell Time

The amount of time that the electron beam is stationary at a point in the digital raster while the BSE signal is acquired and averaged is called the dwell time. Dwell time directly affects analysis time. The GSR sample was analyzcd using dwell times of 4, 16, 64, and 256 μs. The video threshold was set at 100.

The results of the BSE video dwell time experiment are given in Table 3. There is very little difference in the number of Pb-Sb-Ba particles found per field of view (range, 0.23 to 0.28). Note that two to three times as many Pb-Sb-Ba particles were found using

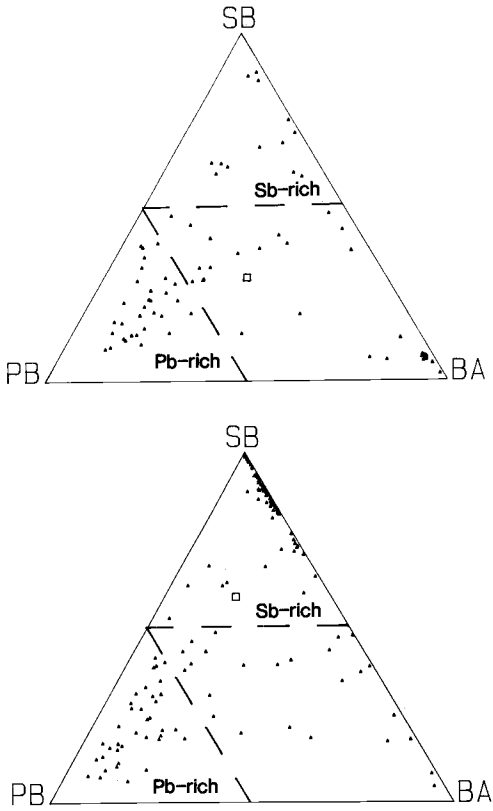

FIG. 4—*Ternary diagrams for Pb-Sb-Ba particles found using BSE thresholds of 75* (top) *and 100* (bottom).

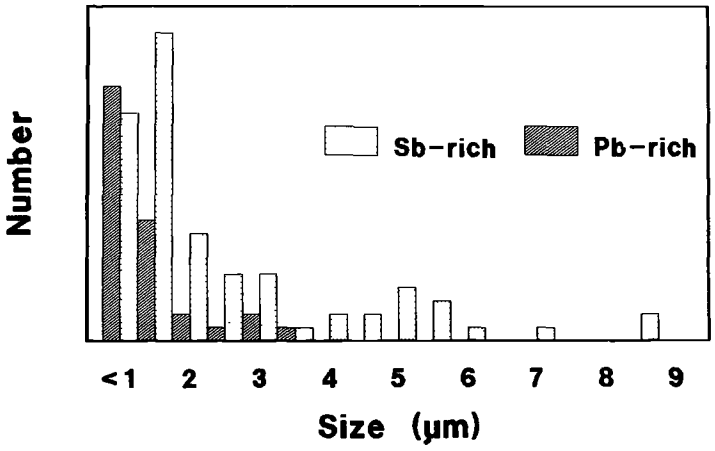

FIG. 5—*Particle size distributions for Pb-rich (Pb RI >0.5) and Sb-rich (Sb RI >0.5) Pb-Sb-Ba particles found using a threshold of 100.*

TABLE 3—*Summary of results from the video dwell time experiment.*[a]

	Dwell Time, μs			
	4	16	64	256
Fields	428	323	396	327
Pb-Sb-Ba particles				
EDX analysis	41	43	35	32
WDX analysis	98	89	97	96
Pb-Sb-Ba particles per field[b]	0.23	0.23	0.24	0.28

[a]The data obtained are for 200 particles at each dwell time.
[b]Based on WDX data only.

WDX analysis than were found using EDX analysis. Also note that the number of Pb-Sb-Ba particles per field is less in this experiment than is shown in Table 2 for a video threshold of 100. The reason for the difference is the fact that the same area of the sample may not have been analyzed for each set of experiments. Therefore, these Pb-Sb-Ba particle loadings indicate the degree of heterogeneity of the GSR sample.

Digital Point Spacing Experiment

The number of points in the digital raster will also affect the sample analysis time. The operator can choose the number of points in the "coarse" and "fine" digital raster. The coarse raster is used to search for particles, while the fine raster is used during particle size analysis. The GSR sample was analyzed for particles greater than 1 μm in diameter using coarse raster point spacings of 1.0, 0.5, and 0.25 μm. The fine raster point spacing was set at one half the distance used for the coarse raster. The results of this experiment are given in Table 4.

As the interpoint spacing decreases, the number of Pb-Sb-Ba particles found increases (0.54 to 1.5 Pb-Sb-Ba particles per field). Also, the average particle size decreases from 5.3 to 2.8 μm when the interpoint spacing decreases from the minimum particle size (1 μm) to a spacing of one half the minimum particle size. The results indicate that an interpoint spacing equal to one half the minimum particle size is needed. However, a smaller interpoint spacing may not be warranted, considering the increase in analysis time. That is, halving the interpoint distance approximately quadruples the time required

TABLE 4—*Summary of results for the coarse raster point spacing experiment.*[a]

	Raster Point Spacing, μm		
	1.0	0.5	0.25
Fields	205	90	72
Pb-Sb-Ba particles			
EDX analysis	71 (5.7)[b]	44 (2.8)	48 (2.6)
WDX analysis	110 (5.3)	101 (2.8)	106 (2.6)
Pb-Sb-Ba particles per field[c]	0.54	1.1	1.5

[a]The data obtained are for 300 particles at each spacing.
[b]The average particle diameters (in micrometres) are in parentheses.
[c]Based on WDX data only.

to scan a field of view. It is interesting to note that the ratio of Pb-Sb-Ba particles found using EDX analysis as opposed to WDX analysis decreases with interpoint distance. This is because of the decrease of the average particle diameter with decreasing interpoint distance. EDX results are better for larger particles.

X-ray Analysis Experiments

The operator has the choice of obtaining EDX/WDX data in either "point" or "raster" mode. In addition, the operator can choose the X-ray analysis time. An experiment was done to evaluate GSR analysis using both point and raster modes. Also, an experiment was done using EDX/WDX counting times of 3, 9, and 27 s. The results of the X-ray analysis mode experiment are shown in Table 5.

The results indicate that there is very little difference between X-ray analyses obtained using the point and raster mode. Evidently the X-ray emission volume for Pb-Sb-Ba particles must be large compared with the average particle size (2.5 to 3.0 μm) so as to eliminate any effects due to chemical heterogeneity of the particles.

The results of the X-ray counting time experiment are given in Table 6. The number of Pb-Sb-Ba particles found per field increases with increasing X-ray counting time. This is due to the improved signal-to-noise ratio for longer counting times. There is a factor-

TABLE 5—*Summary of results for the X-ray analysis mode experiment.*[a]

	X-ray Analysis Mode	
	Point	Raster
Fields	77	78
Pb-Sb-Ba particles		
EDX analysis	42 (2.9)[b]	39 (2.6)
WDX analysis	116 (2.6)	112 (2.7)
Pb-Sb-Ba particles per field[c]	1.5	1.4

[a]The data obtained are for 300 particles in each mode.
[b]The average particle diameter (in micrometres) are in parentheses.
[c]Based on WDX data only.

TABLE 6—*Summary of results for the X-ray counting time experiment.*[a]

	Counting Time, s		
	3	9	27
Fields	80	81	85
Pb-Sb-Ba particles			
EDX analysis	65	98	117
WDX analysis	73	105	151
Pb-Sb-Ba particles per field[b]	0.9	1.3	1.8

[a]The data obtained are for 300 particles at each counting time.
[b]Based on WDX data only.

of-two increase in the number of Pb-Sb-Ba particles found by WDX analysis for a factor-of-nine increase in counting time.

Conclusion

Gunshot residue particles have heterogeneous chemical compositions and range in size from submicrometre to tens of micrometres in diameter. Consequently, developing an automated SEM/GSR procedure can be very difficult. A trade-off has to be made between the analysis time and GSR particle detection.

Proper setting of the BSE video threshold may be the most important factor in obtaining accurate and reproducible GSR particle analyses. A calibrated BSE detector is essential for setting the video threshold. The results of the BSE video threshold experiment indicate that the chemical composition of the GSR particles found depends upon the BSE video threshold used. At lower video thresholds, more small Pb-rich Pb-Sb-Ba particles are found, whereas, at higher video thresholds, larger Sb-rich Pb-Sb-Ba particles are found. A video threshold of 100 is a good compromise for locating Pb-Sb-Ba particles to the exclusion of analyzing environmental (non-GSR) particles. Searching is limited to particles >1.0 μm in diameter. It was demonstrated that Pb-Sb-Ba particles as small as 0.5 μm in diameter can be found by automated analysis. However, the increase in the number of Pb-Sb-Ba particles per field when the submicrometre size range is included may not be worth the increase in analysis time. For example, at a threshold of 100, 30% of the Pb-Sb-Ba particles are submicrometre in size. It would increase the analysis time by a factor of four to search for these particles. The optimum BSE video threshold and minimum particle size will depend to a great extent on the sample. For example, if the sample was collected shortly after a gun was fired, then a high BSE video threshold (for example, 125) and large minimum particle size (for example, 2 μm) might be appropriate. If the sample was collected several hours after firing, then a lower threshold (for example, 75) and smaller minimum particle size (for example, 0.5 μm) might be needed.

A BSE video dwell time of 4 μs is used. Using a shorter dwell time (1 μs being the lower limit for our system) does not significantly change the sample analysis time. A longer dwell time does not significantly increase the number of Pb-Sb-Ba particles detected.

A digital raster interpoint spacing of 0.5 μm (one half the minimum particle size) is used. The number of Pb-Sb-Ba particles detected per field increases (by 40%) if an interpoint spacing of 0.25 μm is used. However, the analysis time increases by at least a factor of four. When using an interpoint spacing of 1.0 μm, the number of Pb-Sb-Ba particles decreases by 50%, with a large change in the average Pb-Sb-Ba particle size (2.8–5.3 μm). Although a 1.0-μm interpoint spacing would decrease the analysis time, it is not used because of the difficulty of detecting smaller GSR particles.

The point mode is used for X-ray acquisition because it provides a threefold higher count rate than does the raster mode. No difference was observed between the point and raster modes for X-ray acquisition in the analysis of Pb-Sb-Ba particles.

The optimum X-ray counting time will strongly depend upon the minimum particle size analyzed and the proportion of GSR particles in a sample. Increasing the X-ray counting time from 3 to 27 s led to an increase of a factor of two in the number of Pb-Sb-Ba particles detected. Because the X-ray counting time directly affects the sample analysis time, the shortest X-ray counting time should be used. However, longer X-ray counting times provide a better signal-to-noise ratio and an improved elemental detection limit, which is especially important with analyzing smaller (submicrometre) GSR particles.

WDX spectrometry has been invaluable for performing the automated SEM/GSR experiments described herein. Wavelength-dispersive X-ray spectrometry eliminates the need to relocate potential GSR particles for detailed manual evaluation of the EDX

spectrum for possible artifacts due to X-ray peak overlaps. The advantage of WDX spectrometry for casework samples, for which the operator must confirm the automated analysis results anyway, is its better sensitivity, which provides identification of more GSR particles than is possible by EDX analysis alone.

The results of this study have demonstrated the effect of several instrumental parameters on automated GSR particle analysis. It would be difficult to specify a set of recommended operating conditions for GSR analysis based on the results obtained from the one sample used in this study. The study does, however, provide a guide for others who may want to optimize their automated GSR particle analyses. Similar studies need to be performed on other GSR samples. With more data it should be possible to develop standard procedures for automated SEM/GSR particle analysis.

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