



Standard Guide for Gunshot Residue Analysis by Scanning Electron Microscopy/ Energy—Dispersive Spectroscopy¹

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1. Scope

1.1 This guide covers the analysis of gunshot residue (GSR) by scanning electron microscopy/energy-dispersive spectrometry (SEM/EDS) by manual and automated methods. The analysis may be performed “manually,” with the operator manipulating the microscope stage controls and the EDS system software, or in an automated fashion, where some amount of the analysis is controlled by pre-set software functions requiring little or no operator intervention.

1.2 Since software and hardware formats vary among commercial systems, guidelines will be offered in the most general terms possible. Each system’s software manuals should be consulted for proper terminology and operation.

2. Referenced Documents

2.1 ASTM Standard:

E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data²

3. Summary of Practice

3.1 Particles composed of high mean atomic number elements are detected by their backscattered electron signals and an EDS spectrum is obtained from each. The elemental profile is evaluated for constituent elements which may identify the particle as being unique to or indicative of GSR.

4. Significance and Use

4.1 This document will be of use to forensic laboratory personnel who are involved in the analysis of GSR samples by SEM/EDS.

4.2 Analysis of GSR by SEM/EDS currently provides a highly definitive method of identification,^{3,4} because it assigns an elemental profile to a particular particle. This contrasts with a bulk sample method, such as atomic absorption or neutron activation analysis, where the total measured levels of the

elements in question are not distinguishable from non-GSR sources.^{3,4}

5. Sample Preparation

5.1 Once the evidence seal is broken, care should be taken so that no object touches the surface of the collection stub and that the specimen stub is not left uncovered any longer than is reasonable for transfer or mounting.

5.2 Label the stub in such a manner that it is distinguishable from other specimen stubs without compromising the sample’s analysis, that is, label the bottom or side of the stub.

5.3 If a non-conductive adhesive was used in the collection device, the sample will need to be coated to increase its electrical conductivity. Carbon is a common choice of evaporant, since it will not be detected with a beryllium window EDS detector and, thus, will not interfere with X-ray lines of interest. A thickness of between 5 and 50 nm is typical, with more non-conductive samples requiring a thicker coat.

6. Sample Area

6.1 Sample stubs for SEMs typically come in one of two diameters: 12.7 mm (0.5 in.) or 25.4 mm (1 in.); these yield surface areas of, respectively, 126.7 mm² and 506.7 mm². To manually analyze the total surface area of the stub is prohibitively time-consuming; since the distribution of particles collected onto an adhesive surface is random and the particles do not tend to cluster,^{4,5} appropriate sampling regimes may be employed.

6.2 This relationship may also be expressed in terms of the portion of the area that must be searched to ensure the finding, with some arbitrary certainty, of at least one GSR particle, based on a predetermined population on a stub:

$$p = 1 - p^{1/N} \quad (1)$$

Thus, for example, if a jurisdiction required the identification of a minimum of 5 GSR particles on a stub for a positive finding for GSR, a search of 45 % of the stub area that yielded no particles would indicate with 95 % certainty that further searching would be unlikely to provide a positive finding. A search of 60 % of the stub with no GSR particles observed

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² *Annual Book of ASTM Standards*, Vol 03.06.

³ Krishnan, S. S., “Detection of Gunshot Residue: Present Status,” *Forensic Science Handbook*, Volume I, Prentice Hall, Inc., Englewood Cliffs, NJ, 1982.

⁴ Wolten, G. M., Nesbitt, R. S., Calloway, A. R., Loper, G. L., and Jones, P. F., “Final Report on Particle Analysis for Gunshot Residue Detection,” *Report ATR-77 (7915)-3*, Aerospace Corporation, Segundo, CA, 1977.

⁵ Halberstam, R. C., “A Simplified Probability Equation for Gunshot Primer Residue (GSR) Detection,” *Journal of Forensic Sciences*, V36, N3, pp. 894–897, 1991.

increases this certainty to 99 %.

7. Operating Parameters

7.1 Scanning Electron Microscope (SEM) Parameters:

7.1.1 Most commercial-grade SEMs should suffice for manual GSR analysis. The SEM/EDS system must, however, meet the following performance specifications:

7.1.1.1 The instrument must be capable, operating in the backscattered mode, of detecting potential GSR particles down to 0.5 μm in diameter.

7.1.1.2 The instrument must be capable, operating with the EDS unit, of producing a signal-to-noise ratio no less than 3:1 for the Pb $L\alpha$ line from a lead particle no greater than 1 μm in diameter.

7.1.1.3 The EDS detector must be capable of resolving clearly the Ba $L\alpha_1$, $L\beta_1$, and $L\beta_2$ peaks.

7.1.2 From a practical standpoint, these performance requirements indicate that the SEM/EDS system must be capable of a minimum accelerating voltage of 20 keV; higher accelerating voltages should result in improved analytical sensitivity. The EDS system will typically have a resolution of less than 150 eV, measured as the full width at half the maximum height of the Mn $K\alpha$ peak; lower resolutions will provide improved discrimination of adjacent and/or overlapping peaks. Display of the EDS output must cover the range of 0-20 keV.

7.2 Energy Dispersive Spectrometry (EDS) Parameters:

7.2.1 Most commercial-grade EDS systems should be adequate for manual GSR analysis, the main requirements being a calibrated, scaled display of energy versus X-ray counts, the ability to identify and label X-ray lines and a facility for hard copy output of the display contents. The detector's resolution should be not worse than 150 eV and should be of a single beryllium window design.⁶ At a minimum; the display should be set to 1024 channels at 20 eV per channel. If the software allows, the EDS display should be set to 2048 channels at 10 eV per channel as this provides greater physical resolution of the X-ray lines.

7.3 Sample Placement:

7.3.1 Each stub location on the microscope stage should be indelibly labeled so that each specimen stub that is placed on the stage can be coded for identification purposes.

7.3.2 A system should be devised so that once a stub has been analyzed and removed from the microscope stage, it can be replaced in the same orientation as before its removal. This may consist of marking the side of each stub and aligning it with marks on the microscope stage or by having stubs that fit into the stage in only one position (for example, stubs with a pin that is a half-circle in cross-section). This facilitates relocating particles if additional analyses are required.

8. Manual Analysis

8.1 *Detection and Calibration*—Particles of GSR are detected by their backscattered electron signal intensity, which is proportional to atomic number. Particles of higher mean atomic

number are brighter than those of lower atomic number composition. The absolute signal intensity a particle produces is also related to the electron beam current and the particle's size. As the beam current increases, the amount of signal each particle produces also increases.⁷

8.1.1 The brightness and contrast settings on the backscattered electron detector determine the limits of detection and discrimination of particles whose mean atomic number exceed the minimum setting but fall below the maximum setting. Controls for the backscattered electron signal should be set on a particulate sample of known origin at the same parameters as will be used for the questioned sample analysis; this calibration sample should, if possible, be in the microscope chamber at the same time as the unknown samples to be analyzed.⁸

8.1.2 The backscattered electron detector's brightness and contrast should be set to include those particles of interest and exclude particles that are not of interest. Typically, high contrast and low brightness settings provide an adequate range between thresholds for ease of detection. If the beam current is changed or drifts, the threshold detection limits, which were based on the previous beam current, may no longer be compatible with the new beam current. Analysis shall not begin until the beam current is stable to within $\pm 1\%$ of its measured value. The beam current may be measured with a Faraday cup, a specimen current meter or by comparing the integrated counts within the same peak in sequentially collected spectra.

8.2 Definition and Classification:

8.2.1 Morphologically, the majority of GSR consists of spheroidal particles between 0.5 μm and 5.0 μm in diameter; the remainder are irregular in shape and vary dramatically from 1 to 100+ μm in size.³ It is not consistent with the mechanisms of GSR formation to find particles with crystalline morphology, that is, defined shapes with sharp corners. Particles having such morphologies would not be classified as GSR regardless of their composition. Since morphology is dependent upon conditions at the time of impact and the distance from point of production to point of impact, it can vary greatly and should therefore be considered only a secondary criterion for identification of GSR.

The most accurate method of identifying GSR is by its elemental content. The following composition has been observed only in particles which are characteristic of GSR:

8.2.1.1 Lead, antimony, barium

8.2.1.2 Antimony, barium⁹

8.2.2 Other elements which may occur include silicon, calcium, aluminum, copper, iron, sulfur, phosphorus, zinc (only if the amount of copper is higher than the amount of zinc), nickel in conjunction with copper and zinc, potassium and chlorine. Particles which have a composition consistent

⁷ Goldstein, J. I., et al., 1981.

⁸ A standard sample should have been prepared and mounted in a manner comparable to the collection method in use by the submitting agency. Preferably, the calibration sample will be a sample of GSR from a known source (caliber of weapon, ammunition manufacturer, number of rounds fired, collected area from shooter); additional environmental particles may be added to ensure the inclusion or exclusion of particular classes of particles.

⁹ Wallace, J. S., and McQuillan, J. "Discharge Residues from Cartridge-Operated Industrial Tools," *Journal of Forensic Science Society*, V24, pp. 495-508, 1984.

⁶ A beryllium window absorbs X-ray energies below about 1.0 keV; therefore, elements below sodium (atomic number 11) are not detected; other window materials may be employed (single window light element detectors).

with GSR but not unique to it will have one of the following elemental profiles:

- 8.2.2.1 Barium, calcium, silicon with a trace of sulfur
- 8.2.2.2 Lead, antimony
- 8.2.2.3 Lead, barium
- 8.2.2.4 Lead
- 8.2.2.5 Barium

8.2.3 Other such analytical categories may be developed by the analyst to aid in the sorting of environmentally or occupationally-produced particles which may be found in a sample.

8.3 *X-Ray Analysis*—For each field of analysis, the operator should record the X and Y coordinates of the stage. Particles whose backscattered electron signal brightness exceeds the desired threshold setting, indicating high atomic number contrast, should be identified. The operator should then collect a spectrum from each detected particle by placing the electron beam in spot mode on the center of the particle or rastering an area completely within the particle's volume. The livetime of the spectral acquisition should be set to accumulate sufficient X-ray counts at the desired count rate to provide an adequate statistical basis for identification of all peaks of interest; for a peak to be considered statistically significant, it should exceed the background signal by three standard deviations or more.⁶ The number of particles at the current stage coordinates for each analytical category should be recorded. The operator should follow other intra-laboratory protocols for documentation as appropriate.

9. Automated Analysis

9.1 Automated analysis of GSR involves some portion of the analysis being controlled by pre-set software functions with

little or no operator intervention. The extent to which the SEM and EDS systems communicate and are integrated varies according to the manufacturers involved and the capabilities of the hardware/software architecture. At a minimum, an automated SEM/EDS system should mimic the capabilities of a system being run manually. It should provide hard copy output and permanent storage for stage X and Y coordinates, field of analysis X and Y coordinates, total number of particles detected, total GSR particles, and net and gross X-ray counts for each peak and/or background-corrected percentages¹⁰ for each element of interest per particle. Confirmation of GSR shall be made by the operator upon relocation of potential GSR particles.

9.1.1 *Confirmation of Automated Analyses*—Confirmation of automated analyses shall be done by manual relocation and hardcopy output of data for sufficient particles to support the instrumental results. The hard copy output should include:

9.1.2 Photomicrographs of GSR particles showing their morphologies (as defined in 8.2).

9.1.3 X-ray spectra of each particle. The elements present should be clearly identified and labeled to confirm the target elements and to document the absence of other major elemental components which may indicate that the particle in question is not GSR.

¹⁰ The background-corrected percentage is a qualitative assessment only. No matrix corrections are necessary. The background-corrected percentage is calculated on a per-particle basis as follows:

$$\frac{(\text{Gross peak element counts} - \text{background counts})}{\text{Total Counts in Spectrum}}$$

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