Robert S. White,[1] *B.S. and Anthony D. Owens,*[2] *M.S.*

Automation of Gunshot Residue Detection and Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis (SEM/EDX)

REFERENCE: White, R. S. and Owens, A. D., **"Automation of Gunshot Residue Detection and Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Analysis (SEM/EDX),"** *Journal of Forensic Sciences,* JFSCA, Vol. 32, No. 6, Nov. 1987, pp. 1595–1603.

ABSTRACT: The identification of gunshot residues (GSR) is generally accomplished by bulk analysis of complete residue samples (by atomic absorption spectroscopy or neutron activation analysis) or by residue particle analysis (by scanning electron microscopy and energy dispersive X-ray analysis). The limitations and advantages of the two techniques are discussed. Two systems for the automation of GSR particle search have become commercially available recently. A detailed operational description and the results of 50 experimental search runs are reported for 1 of these systems. These results are also compared with results of 16 experimental search runs conducted with the second of the automation systems commercially available.

KEYWORDS: forensic science, gunshot residues, microscopy, X-ray analysis, chemical analysis

Forensic scientists currently use two general methods for the detection and identification of gunshot residues (GSR): bulk analysis (which predominates) and particle analysis. The "positive" identification of GSR by both methods relies ultimately on the hypothesis that such residues can be uniquely characterized by elemental composition, usually a combination of barium, antimony, and lead [*1*].

Bulk analysis techniques typically consist of quantitative determinations (in a total residue sample) of barium and antimony by neutron activation analysis or barium, antimony, and lead by atomic absorption spectroscopy. Inherent in the use of these bulk analysis techniques are the following assumptions:

1. The quantitative levels of barium, antimony, and lead are accurately determined.
2. Contributions to the measured total levels of barium, antimony, and lead from non-GSR (for example, environmental) sources are accurately or reliably known.

Although Assumption 1 introduces additional uncertainty (by virtue of the necessity for accurate quantitation), at least the techniques used lend themselves readily to error analysis so that degrees of uncertainty or analysis confidence levels can be established. Unfortunately, as a result of the complexity of the problem, it is not clearly established that Assumption 2

Received for publication 23 Feb. 1987; revised manuscript received 20 March 1987; accepted for publication 21 March 1987.

[1]Lieutenant, West Virginia Police Laboratory, South Charleston, WV.
[2]Applications manager, Gatan, Inc., Warrendale, PA.

has ever been or will ever be reliably satisfied. In practical terms, the failure to satisfy Assumption 2 undoubtedly introduces significant uncertainty in the establishment of meaningful[3] barium, antimony, and lead threshold values. This problem is evident in the findings presented by Wolten et al. [*1*], in which only one half the .38 caliber residues and one fifth the .22 caliber residues, collected promptly after firing, contained antimony levels above the threshold level established by the Bureau of Alcohol, Tobacco, and Firearms. The problems discussed above, coupled with the problem of rapid loss of gunshot residue from the firing hand with time, seriously limit the success rate of bulk analysis techniques.

The use of particle analysis methods to detect the presence of GSR follows logically from the consideration of the theoretical processes involved in residue formation. The discharge of a firearm results in the atomization of molten or vaporized bullet and primer materials or both, which condense rapidly as a result of the sudden temperature quench [*2*]. The process is quite analogous to processes currently used to produce fine superalloy powders for advanced metallurgical applications [*3*]. In both cases, the condensed particles predominantly assume a characteristic spheroidal morphology (which minimizes the surface energy contribution to the total energy of the particle [*4*]). The detection of gunshot residue by particle analysis was first reported by Nesbitt et al. [*5*]. Particulate residues were examined by means of scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Such a combination of techniques has a number of advantages with respect to the identification of GSR:

1. The unique barium, antimony, lead composition characteristic of GSR can be detected using EDX and correlated spatially with a specific particle by SEM.
2. Particles containing the characteristic elemental combination in Ref *1* also commonly possess morphologies (as determined by SEM) consistent with current theoretical models of gunshot residue formation.
3. Elements other than barium, lead, and antimony which are consistent with a GSR identification can be readily detected and identified by EDX (for example, silicon, aluminum, calcium, copper, iron, sulfur, zinc, potassium, chlorine [*1*]).
4. There are no non-GSR sources or processes currently known which result in the formation of fine grained spheroidal particles containing an abundance of barium, antimony, and lead.
5. Particle analysis does not require quantitative elemental analysis, eliminating the threshold problem which severely limits bulk analysis techniques.
6. Elimination of the quantitation/threshold problem increases the probability of GSR detection after larger post-firing collection delays (on the order of hours [*1*]).

Clearly, the method of particle analysis via SEM/EDX is superior to that of bulk analysis as concerns the detection and positive identification of gunshot residue. Unfortunately, the excessive operator time required has deterred its use. To circumvent this problem, a number of timesaving approaches have been taken, such as the use of statistical considerations to reduce the "necessary" specimen search area [*1*], and various residue collection and concentration techniques to improve collection efficiency and reduce levels of extraneous particulates [*6–8*]. A further step in this direction is the development of microprocessor controlled systems which would automate the GSR search and identification process. Such an automation system has four advantages over a manual search procedure:

- total search times could be reduced or total searched areas could be increased or both,
- SEM/EDX operators are freed to perform other tasks,
- an automated system could run unattended overnight, freeing the SEM/EDX instrumentation for other forensic science tasks during the day, and

[3]Meaningful with respect to the identification of barium, antimony, and lead levels indicative of a probable GSR origin.

- an automated system would reduce human sources of analysis bias and error (for example, errors as a result of operator fatigue and distraction, and variabilities among different operators).

In summary, it is clear that the use of an automated particle analysis system using SEM/EDX instrumentation could significantly improve the success of GSR searches and the confidence in search procedures and conclusions. Two such automation systems have recently been made commercially available [*9-11*]. The remainder of this paper is devoted to a detailed description of one of the available systems [*10,11*], including the results of a series of experimental search runs conducted by one of the authors (RSW) at the Department of Public Safety, Charleston, West Virginia. A comparison of the two automated particle analysis systems is also given.

Instrumentation

The automation system described is designed and manufactured by the Cambridge Scanning Company Ltd.[4] The complete system includes the following instrumentation:

- Cambridge Scanning Co. Camscan S2 or S4 SEM, with motorized stage drives and GSR automation system hardware,
- backscattered electron detector operable at TV scanning rates, and
- conventional energy-dispersive X-ray analyzer.

Principles of Operation

Sampling and Search Coordinates

Residue samples are collected by any of the commonly used adhesive lift or concentration techniques and fixed to a standard SEM mount (carbon or aluminum, 1/8-in. (0.3-cm) pin by 1/2-in. (1.3-cm) diameter surface or greater). The searched area for a single specimen is approximately 120 mm^2 (12 by 10 mm), and up to four specimens can be accommodated for automated sequential searches (Fig. 1). Each 120-mm^2 search area is divided into a 16-by-16 matrix of 256 motor (M) spaces, so called because each is selected for imaging or searching purposes by means of automated stage motions. In addition, each motor space is divided into 256 (16-by-16) electronic (E) spaces, each of which is selected by means of automated electron beam positioning. Thus, each specimen is divided into 65 536 independent E-spaces which are searched by a combination of automated stage and e-beam positioning, and which provide a relatively high resolution coordinate system to define GSR locations. A small amount of overlap between each E-space and its neighbors ensures total search coverage of each specimen.

GSR Search Method

The detection and positive identification of GSR is accomplished in a two-stage process similar to that described by Wolten et al. [*1*] and Tillman [*9*]. Each E-space is scanned in sequence while simultaneously monitoring the signal level from a backscattered electron (BSE) detector. The scan raster structure is designed to detect particles with a diameter of 0.5 μm or greater.

Since the backscattered electron signal intensity increases with increasing atomic number [*12*], particles with high BSE intensities are potentially GSR particles, which have high aver-

[4]Saxon Way, Bar Hill, England CB3 8SL, represented in the U.S. by Gatan, Inc., Trading Division, 780 Commonwealth Drive, Warrendale, PA 15086.

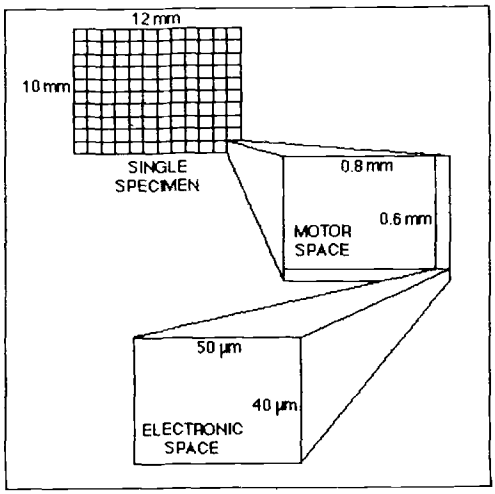

FIG. 1—*Coordinate system used for automated GSR search.*

age atomic numbers. Since BSE signals are relatively intense, this stage of the search can be performed at near-TV scan rates provided a suitable BSE detector is used. The detection of potential GSR initiates the second stage of the search process, in which the e-beam is confined to the position of the particle. Positive identification of the particle is then determined by monitoring background corrected X-ray signals for each element barium, antimony, and lead. The location coordinates (specimen No., M-space, E-space) of positive GSR are then stored for subsequent operator viewing and verification and may be output to a printer if desired. The operator can also configure the system to locate alternate classes of particles, for example, any particle containing any combination of two of the three elements. In the interest of saving time, the remaining search of an E-space is abandoned once a positive GSR identification has been made in that coordinate (since one E-space coordinate is the maximum resolution with which a particle's location can be defined).

No morphological criteria are used to identify a particle as positively gunshot residue. Such morphological analysis would introduce unacceptable increases in search and identification times. Also, GSR formation is a complicated, nonequilibrium process resulting in residue compositions and morphologies which can and do vary from the ideal situation of barium, antimony, lead spheroids [*2,6*]. Thus, although spheroidal morphology may be common in gunshot residue and consistent with a GSR identification, it certainly is not unique to GSR nor a ubiquitous GSR characteristic. Because of the time involved, any morphological analysis is most efficiently done after the identification of chemically unique GSR particles.

The entire search process is directed through a small control module which provides the operator with a specimen coordinate display as well as a display of the number of GSR particles identified. The controller allows automatic sequential selection of all E-spaces containing positively identified GSR, or operator selection of any one of the 65 536 E-space coordinates (on any of the four specimens) to be scanned. After selection, the E-space is automatically imaged, and the operator may photograph or analyze by EDX a magnified portion of the E-space. An automated search may be interrupted by the operator at any time for a visual/analytical review of identified particles and then resumed at the point of interruption.

Operating Conditions

The SEM and EDX operating conditions used with GSR automation are listed in Table 1. Since virtually any conventional EDX system can be used, only general EDX operating parameters are given.

Estimated Search Times

Since the electron beam is scanned and the BSE detector operated, at near-TV rates, the search time for a sample is dominantly controlled by the X-ray analysis stage of the identification process. This is easy to understand when one considers that the rate at which signal carriers are generated in the specimen is less for X-ray photons than for backscattered electrons by four to five orders of magnitude. Since X-ray photons must be collected only for potential GSR particles, the search time varies rapidly as a function of the BSE intensity threshold which defines potential GSR, as well as the number of particles with BSE intensities above this threshold. Note that this limitation is not restricted to the automated search, but applies equally to a manual SEM/EDX search which relies on the same basic GSR detection/identification scheme. The estimated automated search time for a 120-mm^2 search area is shown as a function of potential GSR particle number density (number of particles/mm^2) in Fig. 2[5] (Curve A). Although potential GSR particle number densities must vary considerably in actual casework, experiments conducted for this paper (discussed in more detail later) as well as the data of Tillman [*9*] suggest that values in the range of 10 to 100 particles/mm^2 are common. These values correspond to a range of estimated search times of 3 to 8 h for complete coverage of a 120-mm^2 sample.

Experimental Results

The statistical results of 40 experimental GSR searches, conducted by R. S. White at the West Virginia Department of Public Safety, are discussed in the following paragraphs. Test firings were made in an indoor firing range using a variety of firearms, including a .357 revolver, .32 revolver, .38 revolver, .25 automatic, .45 automatic, .22 NAA mini revolver, .22 rifle, .223 auto rifle, 9-mm Colt auto machine gun, 12-gage shotgun, and 28-gage shotgun. Residues were collected at postfiring time intervals of 0 to 6 h using Scotch 666 double-sided tape on SEM mounts and coated with carbon in a vacuum evaporator. All samples were

TABLE 1—*Operating conditions for SEM and EDX.*

Condition	Range
SEM:	
Accelerating voltage	25 kV
Working distance	30–35 mm
Specimen tilt	0–20°
Magnification	×1800 (nominal, referenced to Polaroid 545 format film size 4 by 5 in. [10 by 13 cm])
Beam current	1 nA (nominal)
EDX:	
X-ray acquisition energy range 0–20 keV	
X-ray lines monitored SbLa, BaLa, PbLa	

[5]Based on E-space frame time, 130 ms, and X-ray acquisition time per potential GSR particle, 2 s.

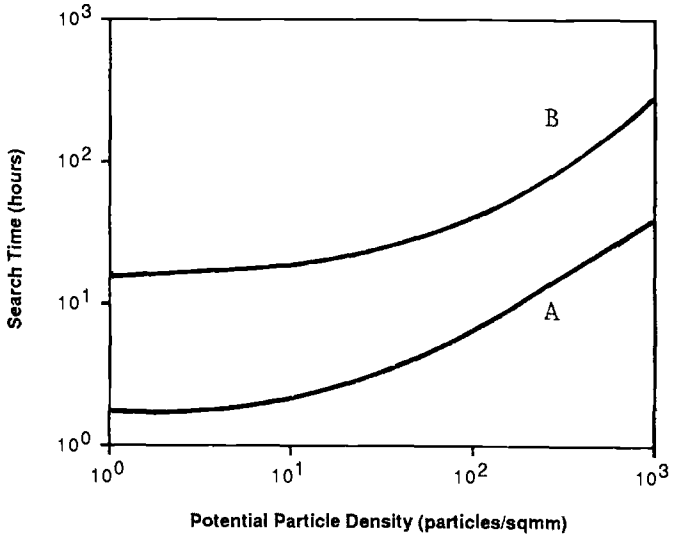

FIG. 2—*Computed estimate of search time as a function of potential GSR particle number density for a 120-mm² search area. Curve A, present study; Curve B, computed from data of Tillman* [9].

obtained from the back of the firing hand, concentrating on the thumb, web area, and index finger until the adhesive stickiness was gone. Statistical data from the 40 experimental searches are presented in Table 2. Complete 120-mm² searches were rarely required as a result of the abundance of GSR particles.

The number of unique GSR particles identified ranged from 0 to 57 in single runs, with an average of 13 GSR particles (0 GSR particles were found in 5 of the 40 runs). The average search time was 72 min for an average searched area of approximately 43 mm² (91 M-spaces or 23 300 E-spaces). Figure 3 is a plot of search time required as a function of searched area (in terms of M-spaces). A significant degree of scatter in the plot indicates that factors other

TABLE 2—*Statistical results of 40 experimental automated GSR searches.*[a]

Result
Number experimental runs (N) = 40
Average search time per run ($\bar{t}$) = 72 min (σ = 36 min)
Average number M-spaces searched per run ($\bar{M}$) = 91 (σ = 63)
Average search time per M-space ($\bar{t}_M$) = 1.4 min (σ = 1.6 min)
Average number unique GSR particles identified per run = 13 (σ = 16, range = 0-57)

[a]Average values computed as follows:

$$\bar{t} = \sum_{i=1}^{N} t_i/N, \text{ where } t_i = \text{time for run } (i),$$

$$\bar{M} = \sum_{i=1}^{N} M_i/N, \text{ where } M_i = \text{number M-spaces for run } (i), \text{ and}$$

$$\bar{t}_M = \sum_{i=1}^{N} (t_i/M_i)/N.$$

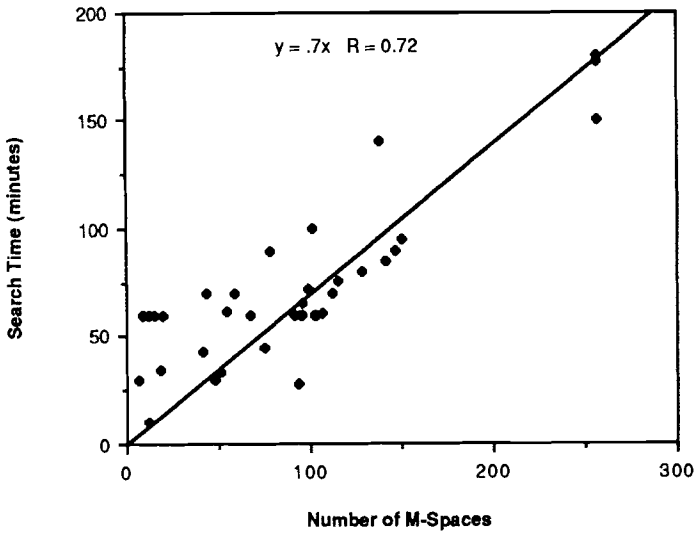

FIG. 3—*Experimental search times as a function of search area (in units of M-spaces).*

than search area affect search time. The most important factors are BSE detector setting variations (brightness and contrast), abundance of high atomic number particles, and variations in beam current. Nonetheless, an analytical estimate of search time versus search area can be obtained by least-squares linear regression with the additional constraint that the function so obtained passes through the origin. The function obtained (drawn in Fig. 3) suggests search times for a complete 120-mm^2 sample (256 M-spaces) on the order of 200 min. Using this value and referring again to Fig. 2, we can estimate the average potential GSR particle number density to be on the order of 20 to 30 particles/mm^2.

Control Experiments

In addition to the forty experimental runs above, a number of control experiments were conducted. Five specimens were collected from five individuals who had not discharged a firearm. Two other specimens consisted of a cleaned carbon SEM mount and a fresh polyester filter fixed to a SEM mount with carbon dag. Four additional specimens were prepared by allowing SEM mounts (with double-sided tape) to stand in air for 72 h in various rooms of the West Virginia Department of Public Safety. The firing range was one of the rooms used. As one might expect, on this sample unique GSR particles were identified. However, no unique GSR particles were identified during automated searches of the other ten specimens.

Comparison with Other Automated GSR Particle Search Systems

As far as the authors know, only one other automated SEM/EDX particle analysis system has been reported for the purpose of gunshot residue detection [*9*]. The system used was, in general, similar to that reported here, using an SEM with a BSE detector for locating potential GSR, and an EDX system for positive GSR identification. The data presented by Tillman [*9*] are plotted in Fig. 4, showing search time as a function of total number of potential GSR particles (defined exactly as in this paper—that is, particles with BSE intensities high enough to justify an X-ray analysis). Also shown is the analytical function obtained by a linear least squares analysis of the data. Given the total search area (4 mm^2 for each of the

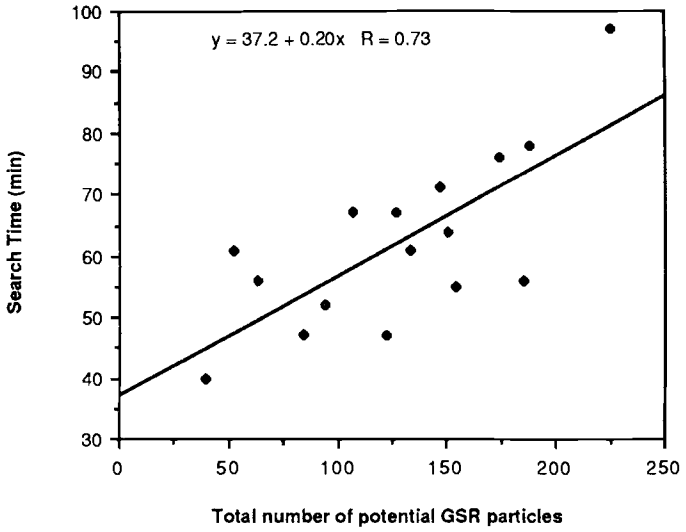

FIG. 4—*Data of Tillman* [9] *plotted as experimental search times as a function of the total number of potential GSR particles in the search area.*

sixteen experimental runs of Tillman), the data can be extrapolated to estimate search time as a function of potential GSR particle number density for a 120-mm^2 search area. The relationship obtained is plotted in Fig. 3 (Curve B), indicating search times nearly one order of magnitude longer than for the system reported in this paper. The data of Tillman also allow an estimate of the average potential GSR particle number density. Particle number densities from the 16 runs average approximately 30 particles/mm^2 (range 0 to 60/mm^2), consistent with the values estimated from the present study (20 to 30/mm^2). Therefore, it is unlikely that this factor is responsible for the large difference in search time requirements for the two systems. The difference is more likely attributed to the use of slow scan rates (rather than near-TV rates), longer maximum X-ray acquisition times, and morphological criteria in the GSR identification process in the system used by Tillman. Differences in methods of signal processing and the uses of software versus hardware could also account for the search time difference.

Conclusions

The technique of particle analysis (via SEM/EDX) presents a number of advantages over bulk residue analysis (via atomic absorption spectroscopy/neutron activation analysis [AAS/NAA]) in the detection and positive identification of gunshot residue. Automation of the particle analysis technique provides additional advantages over a manual procedure, especially in the analysis time requirement, which has been a major deterrent to the use of this technique. As a result, two systems are now commercially available which automate the GSR particle search process using SEM/EDX instrumentation. Results of the experimental use of both systems have now been presented in the literature; they indicate that automated SEM/EDX particle analysis is a reliable technique for the detection of gunshot residue. Although the general scheme of search, initial detection, and positive identification of GSR are similar for the two automation systems, the time requirements for analysis appear to differ significantly, presumably as a result of differences in instrumentation and processing methods.

Acknowledgments

The authors wish to thank Pete Burgner, Ron Zolkowski, and Larry Stoter, Gatan, Inc., for their assistance in the preparation of the computer generated figures, and Susan Thompson for her assistance in the preparation of the manuscript.

References

[1] 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, The Aerospace Corp., Sept. 1977.

[2] Basu, S., "Formation of Gunshot Residues," *Journal of Forensic Sciences,* Vol. 27, No. 1, Jan. 1982, pp. 72-91.

[3] Kear, B. H., "Advanced Metals," *Scientific American,* Vol. 255, No. 4, Oct. 1986.

[4] Atkins, P. W., *Physical Chemistry,* 2nd ed., Oxford University Press, U.K., 1982.

[5] Nesbitt, R. S., Wessel, J. E., and Jones, P. F., "Detection of Gunshot Residue by Use of the Scanning Electron Microscope," *Journal of Forensic Sciences,* Vol. 21, No. 3, July 1976, pp. 595-610 (originally published as Report ATR-75 (7915)-2, The Aerospace Corp., Dec. 1974).

[6] Wallace, J. S. and Keeley, R. H., "A Method for Preparing Firearms Residue Samples for Scanning Electron Microscopy," *Scanning Electron Microscopy,* Vol. 2, 1979, pp. 179-184.

[7] Basu, S. and Ferriss, S., "A Refined Collection Technique for Rapid Search of Gunshot Residue Particles in the SEM," *Scanning Electron Microscopy,* Vol. 1, 1980, pp. 375-384.

[8] Sugarman, L., "The Concentration and Isolation of Gunshot Residues for Particle Analysis," Report B57, American Academy of Forensic Sciences 39th Annual Meeting, San Diego, CA, Feb. 1987.

[9] Tillman, W. L., "Automated Gunshot Residue Particle Search and Characterization," *Journal of Forensic Sciences,* Vol. 32, No. 1, Jan. 1987, pp. 62-71.

[10] White, R. S., "Automatic Gunshot Residue Analysis and a Dual Scanning System by Scanning Electron Microscopy," Report B48, American Academy of Forensic Sciences 38th Annual Meeting, New Orleans, LA, 1986.

[11] Owens, A. D. and White, R. S., "Advanced SEM Instrumentation for Microscopic Comparisons and Automated Gunshot Residue Analysis," Combined Meeting of the Southern, Midwestern, Mid-Atlantic, Northeastern, and Southwestern Associations of Forensic Scientists, Lexington, KY, May 1986.

[12] Goldstein, J. I., Newbury, D. E., Echlin, P., Joy, D. C., Fiori, C., and Lifshin, E., *Scanning Electron Microscopy and X-Ray Microanalysis,* Plenum Press, New York, 1981.

Address requests for reprints or additional information to
Robert S. White, Lt.
West Virginia State Police
725 Jefferson Road
South Charleston, WV 25309