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## **Forensic Science**

### **Gunshot Residue Tests**

## By Paul C. Giannelli\*

Determining whether a person has recently fired a weapon may be of critical importance in identifying an assailant, proving or rebutting a selfdefense claim, or distinguishing a suicide from a homicide. Consequently, a number of techniques designed to detect gunshot residues (GSR) on the hands of a suspect<sup>1</sup> or victim have been developed.<sup>2</sup> These techniques

' Obtaining GSR from a suspect may raise constitutional issues. In State v. Ulrich, 187 Mont. 347, 609 P.2d 1218 (1980), the court held that taking residue samples at the time of arrest did not violate the Fourth Amendment prohibition against unreasonable searches and seizures, the Fifth Amendment prohibition against self-incrimination, or the Sixth Amendment right to counsel. See also State v. Odom, 303 N.C. 163, 277 S.E.2d 352 (admission of evidence of the defendant's refusal to provide GSR samples did not violate the right to counsel or due process), cert. denied, 454 U.S. 1052 (1981).

<sup>2</sup> See generally Kilty, "A Review of the FBI Laboratory's Gunshot Primer Residue Program," 13 Crime Lab. Digest 54 (April 1986); Krishnan, "Detection of Gunshot Residue: Present Status," in *Forensic Science Handbook* 572 (R. Saferstein ed. 1982); Midkiff, "Detection of Gunshot Residues: Modern Solutions for an Old Problem," 3 J. Police Sci. & Ad. 77 (1975); Annotation, "Admissibility, in Criminal Case, of Results of Residue Detection Test to Determine range from the now-discredited paraffin test to the more modern techniques, which use instrumental analysis or scanning electron microscopy.<sup>3</sup>

All GSR techniques have limitations. First, the residues can be removed by rubbing or washing the hands and, thus, usually must be collected soon after the firearm is fired.<sup>4</sup> This also means that the absence of residues is not very probative. Second, even valid GSR tests are not conclusive:

The real value of the GSR test is that it can associate an individual with a firearm. It is important, however, to note that this does not identify that person as the shooter. GSR can settle on any hand placed near a weapon as it is fired. A person can pick up GSR simply by handling a dirty weapon or discharged ammunition components.

Whether Accused or Victim Handled or Fired Gun," 1 A.L.R. 4th 1072 (1980).

<sup>3</sup> Several other techniques have been reported. E.g., Nesbitt, Wessel, Wolten & Jones, "Evaluation of a Photoluminesence Technique for the Detection of Gunshot Residue," 22 J. Forensic Sci. 288 (1977); Sen, Panigrahi, Rao, Varier, Sen & Mehta, "Application of Proton-Induced X-Ray Emission Technique to Gunshot Residue Analyses," 27 J. Forensic Sci. 330 (1982).

<sup>4</sup> See Kilty, "Activity After Shooting and Its Effect on the Retention of Primer Residue," 20 J. Forensic Sci. 219, 230 (1975) ("[a]s the time after the shooting passes, the possibility decreases that significant amounts of [antimony] and [barium] will be detected").

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It is also possible, but very unlikely, that residue would be deposited on hands by other means.<sup>5</sup>

#### Paraffin Test

The paraffin or dermal nitrate test was introduced in this country in the early 1930s and adopted quickly by law-enforcement agencies.<sup>6</sup> The test is designed to detect the presence of nitrate residues, which, due to the backblast of gases that escape during discharge, may be deposited on the hand of the person firing the weapon. These substances are residues from smokeless powder, the propellant used in modern cartridges. The term "paraffin test" derives from the paraffin cast technique, which is used to remove the residues from the hands. After removal, the cast is tested with a reagent, either diphenylamine or diphenylbenzidine. A color reaction-"dark blue spots"-indicates the presence of nitrate residues.

The principal problem with the paraffin test is its nonspecificity. A significant number of substances other than gunpowder residues contain nitrates and, therefore, also produce a positive reaction. One study concluded that a positive reaction is produced by tobacco or tobacco ash, fertilizer, pharmaceuticals, leguminous plants, and urine.<sup>7</sup> A more comprehensive study found that " 'rust,' colored fingernail polishes, residue from evaporated urine, soap and tap

water<sup>''8</sup> all produce a positive reaction. In other words, the test detects nitrate residues, but the source of these residues cannot be determined. Consequently, the probative value of a positive reaction is marginal at best, and, therefore, the paraffin test is rarely used today. If, however, a positive reaction is accompanied by microscopic identification of gunpowder particles, the nonspecificity problem may be overcome.<sup>9</sup>

The first reported case admitting testimony based on the paraffin test was decided in 1936.<sup>10</sup> In 1959, the first case rejecting the test was reported.<sup>11</sup> Although several courts followed suit and also rejected the paraffin test,<sup>12</sup> evidence based on this test continued to be admitted in other courts.<sup>13</sup> Indeed, in 1979, the Oklaho-

<sup>9</sup> E.g., State v. Fields, 434 S.W.2d 507, 516 (Mo. 1968); Commonwealth v. Westwood, 324 Pa. 289, 300, 188 A. 304, 309 (1936).

<sup>10</sup> Commonwealth v. Westwood, 324 Pa. 289, 188 A. 304 (1936).

<sup>11</sup> Brooke v. People, 139 Colo. 388, 339 P.2d 993 (1959).

<sup>12</sup> See Born v. State, 397 P.2d 924, 939 (Okla. Crim. App. 1964), *cert. denied*, 379 U.S. 1000 (1965); Clarke v. State, 218 Tenn. 259, 270, 402 S.W.2d 863, 869, *cert. denied*, 385 U.S. 942 (1966). See also Fowler v. State, 512 P.2d 238, 244 (Okla. Crim. App. 1973) ("zinc oxide" test for gunshot residue inadmissible).

Both *Born* and *Fowler* were overruled in Brookins v. State, 602 P.2d 215, 217 (Okla. Crim. App. 1979).

<sup>13</sup> See Harris v. State, 239 Ark. 771, 778, 394 S.W.2d 135, 140 (1965), *cert. denied*, 386 U.S. 964 (1967); State v. Hoy, 199 Kan. 340, 348, 430 P.2d 275, 281, (1967); People v. Simpson, 5 Mich. App. 479, 486–487, 146 N.W.2d 828, 831 (1966); State v. Fields, 434 S.W.2d 507 (Mo. 1968); Henson v. State, 159

<sup>&</sup>lt;sup>5</sup> Aaron, "Gunshot Primer Residue: The Invisible Clue," 60 FBI Law Enforcement Bull. 19, 21 (June 1991).

<sup>&</sup>lt;sup>6</sup> See "Diphenylamine Test for Gun Powder", 4 FBI Law Enforcement Bull. 5 (1935) ("current widespread use").

<sup>&</sup>lt;sup>7</sup> Turkel & Lipman, "Unreliability of Dermal Nitrate Test for Gunpowder," 46 J. Crim. L., Criminology & Police Sci. 281, 282 (1955).

<sup>&</sup>lt;sup>8</sup> Cowan & Purdon, "A Study of the 'Paraffin Test,' "12 J. Forensic Sci. 19, 23 (1967).

ma Court of Criminal Appeals overruled an earlier decision and held evidence based on the test admissible, at least where the result of the test is negative.<sup>14</sup>

#### Harrison-Gilroy Test

In 1959, Harold Harrison and Robert Gilroy, of the University of Rhode Island, developed a new chemical method (color test) for GSR detection.<sup>15</sup> Unlike the paraffin test, which detected propellant residues, this test is designed to detect primer residues-antimony, barium, and lead. Accordingly, the presence of nitrates is immaterial, and the nonspecificity of that substance, the principal problem with the paraffin test, is avoided. In addition, the simplicity of the Harrison-Gilrov test made it suitable for field use. Nevertheless, it is not widely used today due to its inadequate sensitivity and other drawbacks.<sup>16</sup> Today, the test is important primarily because it focused attention on primer residues rather than powder residues.

Few reported cases consider the admissibility of evidence based on the Harrison-Gilroy test. In one case, the court excluded evidence of the

Tex. Crim. 647, 655-656, 266 S.W.2d 864, 869 (1953). See also United States v. Snook, 31 C.M.R. 199, 203 (C.M.A. 1962) (paraffin test was negative); State v. Foster, 44 Haw. 403, 354 P.2d 960 (1960).

<sup>14</sup> Brookins v. State, 602 P.2d 215, 217 (Okla. Crim. App. 1979).

<sup>15</sup> Harrison & Gilroy, "Firearms Discharge Residues," 4 J. Forensic Sci. 184 (1959).

<sup>16</sup> See Krishnan, note 2 *supra*, at 574 ("[t]his method did not gain wide acceptance in crime laboratories for field use because of a lack of specificity of the color reaction for the trace elements, inadequate sensitivity, interference of the color reactions among the three elements themselves, and the instability of the colors developed"). test because the analyst modified the test procedure.<sup>17</sup> In another case, the evidence was admitted but the court apparently believed it was considering the paraffin test, which it had earlier approved.<sup>18</sup>

#### Neutron Activation Analysis

Neutron activation analysis (NAA) is a qualitative and quantitative method for determining the elemental composition of substances. It is extremely sensitive and accurate, capable of detecting elements in the microgram and nanogram range. In the detection of GSR, NAA is used to detect the presence and quantity of antimony and barium on the back of the shooting hand.<sup>19</sup> These elements are the primer constituents of many cartridges, and their presence in elevated concentrations on the hands is indicative of a recent discharge of a firearm. Since barium and antimony may be present on the hands of persons who have not fired a firearm. NAA is based on the detection of significantly greater amounts of these elements than normally occur:

The presence of [antimony and barium] together and in amounts significantly higher than those normally found on the hands of the general population (hand blanks) is taken as indicative of the presence of GSR. Hand blank levels have been collected and reported by a number of laboratories. The

<sup>18</sup> Commonwealth v. Farrior, 446 Pa. 31, 34, 284 A.2d 684, 685 (1971).

<sup>19</sup> See Midkiff, note 2 *supra*, at 78– 79; Krishnan, "Detection of Gunshot Residues on the Hands by Trace Element Analysis," 22 J. Forensic Sci. 304, 306 (1977); Comment, "The Evidentiary Uses of Neutron Activation Analysis," 59 Cal. L. Rev. 997, 1074–1078 (1971).

<sup>&</sup>lt;sup>17</sup> State v. Smith, 50 Ohio App. 2d 183, 193–194, 362 N.E.2d 1239, 1246 (1976).

actual levels depend on the area of the hands sampled and to some extent on the sampling method used.<sup>20</sup>

Several methods, including swabbing and washing techniques, have been used to remove residues from the hands. The principal disadvantage of NAA is the required access to a research nuclear reactor.

A number of courts have admitted GSR testimony based on NAA.<sup>21</sup> In one case, however, the court criticized the expert for overstating the conclusions that can be drawn from the test:

We are concerned . . . about the sweeping and unqualified manner in which [the expert's] testimony was offered. . . . An expert witness could be permitted to testify that in his opinion the chemicals pres-

<sup>20</sup> Krishnan, note 2 *supra*, at 579– 580. See also Havekost, Peters & Koons, "Barium and Antimony Distributions on the Hands of Nonshooters," 35 J. Forensic Sci. 1096 (1990).

<sup>21</sup> See Mills v. State, 476 So. 2d 172, 176-177 (Fla. 1985), cert. denied, 475 U.S. 1031 (1986); Troedel v. State, 462 So. 2d 392, 396 (Fla. 1984); State v. Boyer, 406 So. 2d 143, 146-148 (La. 1981); Kelly v. State, 16 Md. App. 533, 535-536, 544-545, 298 A.2d 470, 472, 477, aff'd, 270 Md. 139, 310 A.2d 538 (1973); State v. Spencer, 298 Minn. 456, 459-462, 216 N.W.2d 131, 134-135 (1974); State v. Jackson, 566 S.W.2d 227, 228-229 (Mo. App. 1978); State v. Major, 564 S.W.2d 79, 81-82 (Mo. App. 1978); State v. Montgomery, 545 S.W.2d 655, 655-656 (Mo. App. 1976); State v. Duncan, 540 S.W.2d 130, 134-135 (Mo. App. 1976) (shotgun residue); People v. Pieropan, 72 Misc. 2d 770, 340 N.Y.S.2d 31 (1973); Commonwealth v. Sero, 478 Pa. 440, 449-450, 387 A.2d 63, 68 (1978).

See also United States v. Barton, 731 F.2d 669, 671–672 (10th Cir. 1984) (unspecified "primer residue test" admitted). ent on defendant's hand may have resulted from the firing of a gun. He should not have been permitted to state, as he did, that this defendant had definitely fired a gun.<sup>22</sup>

#### Atomic Absorption

Flameless atomic absorption spectroscopy (FAAS) is another instrumental technique used for elemental analysis. In the detection of GSR, FAAS is used to detect the elements antimony, barium, and lead. The greater availability of this technique and its capability of detecting lead, in comparison to neutron activation analysis, have made it an attractive method for analyzing GSR.<sup>23</sup> Several courts have admitted expert testimony, based on this technique, in GSR cases.<sup>24</sup>

#### Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) is a relatively new method

<sup>22</sup> State v. Spencer, 298 Minn. 456, 461, 216 N.W.2d 131, 134 (1974).

<sup>23</sup> See Midkiff, note 2 *supra*, at 80– 82; Krishnan, "Detection of Gunshot Residue on the Hands by Neutron Activation and Atomic Absorption Analysis," 19 J. Forensic Sci. 789 (1974); Newton, "Rapid Determination of Antimony, Barium, and Lead in Gunshot Residue Via Automated Atomic Absorption Spectrophotometry," 26 J. Forensic Sci. 302 (1981).

<sup>24</sup> See Chatom v. State, 348 So. 2d 838, 842 (Ala. 1977); Bell v. State, 339 So. 2d 96, 99 (Ala. Crim. App. 1976); State v. Chatman, 156 N.J. Super. 35, 37-40, 383 A.2d 440, 441-442 (App. Div. 1978); State v. Crowder, 285 N.C. 42, 53-55, 203 S.E.2d 38, 46-47 (1974), modified on other grounds, 428 U.S. 903 (1976); State v. Sparks, 297 N.C. 314, 326-328, 255 S.E.2d 373, 381-382 (1979); State v. McCall, 698 S.W.2d 643, 651 (Tenn. Crim. App. 1985).

for detecting GSR.<sup>25</sup> It provides a simultaneous qualitative and quantitative method for detecting copper, lead, and antimony. Its principal advantage over other GSR techniques is that it uses inexpensive equipment. ASV is also quick, simple, and nondestructive. Whether ASV alone is sufficient for the detection of GSR is questionable. This technique does not detect barium, a primer residue, used in other instrumental GSR techniques. Proponents of this method rely primarily on the presence of antimony: "Antimony, ... even in trace amounts, is indicative of probable contact with a handgun."<sup>26</sup> Several Missouri cases have admitted evidence based on ASV, but defense

Choucholy & Briner, 'An Inexpensive Approach to Inorganic Gunshot Residue Analysis Using Anodic Stripping Voltammetry,'' 4 Current Separations 20, 20 (1982).

<sup>26</sup> *Id.* See also Brihaye, Machiroux & Gillain, "Gunpowder Residues Detection by Anodic Stripping Voltammetry," 20 Forensic Sci. Int'l 269, 271 (1982); Liu, Lin & Nicol, "The Application of Anodic Stripping Voltammetry to Forensic Science. II. Anodic Stripping Voltammetric Analysis of Gunshot Residues," 16 Forensic Sci. Int'l 53 (1980); Liu & Lin, "The Application of Anodic Stripping Voltammetry to Forensic Science. I. The Construction of a Low-Cost Polarograph," 16 Forensic Sci. Int'l 43 (1980).

experts apparently did not testify in these cases.<sup>27</sup>

#### Scanning Electron Microscopy

The scanning electron microscope (SEM) uses a high-energy electron beam to produce magnification significantly greater than that which is possible with an optical microscope.<sup>28</sup> This increased magnification, as well as greater depth of field, permits the identification of gunshot particles by their characteristic morphology. In addition, scanning with an electron beam causes the emission of X rays. Since each element produces characteristic X rays, an elemental analysis of the substances under examination is possible through the use of energy-dispersive X-ray analysis (EDXA). Barium, antimony, and lead are the elements that are indicative of a firearm discharge. In sum, SEM permits the identification of gunshot particles by their unique morphological characteristics and by elemental analysis.

The principal disadvantages of this technique are the cost of the instruments and the time-consuming nature of the analysis. Other reported problems concern the "variation between laboratories in determining the minimum number of particles analyzed to confirm gunshot residue" and the fact that cigarette lighter flint particles "mimic GSR in morphology."<sup>29</sup>

<sup>28</sup> Judd, "Scanning Electron Microscopy as Applied to Forensic Evidence Analysis," in *Practising Law Institute*, *Scientific and Expert Evidence* 873, 878– 880 (2d ed. 1981).

<sup>29</sup> DeGaetano & Siegel, "Survey of Gunshot Residue Analysis in Forensic Science Laboratories," 35 J. Forensic Sci. 1087, 1090, 1092 (1990).

<sup>&</sup>lt;sup>25</sup> Two authors described the theory underlying ASV as follows:

In the ASV method, metals are preconcentrated (reduced) from an electrolyte solution in a thin-film of mercury which has been deposited on a carbon-based electrode. The metals are then "stripped" (oxidized) from the mercury layer by changing the applied potential on the electrode. Since each metal has a characteristic potential at which it strips from the mercury layer and since the current required to remove the particular amount of metal from the mercury film is proportional to the original concentration, both qualitative and quantitative information can be obtained from a single experiment.

<sup>&</sup>lt;sup>27</sup> State v. Cooper, 691 S.W.2d 353 (Mo. App. 1985); State v. Williams, 659 S.W.2d 309, 310–311 (Mo. App. 1983); State v. Walker, 654 S.W.2d 129, 131– 132 (Mo. App. 1983).

Although the use of this technique for the detection of GSR is recognized in the literature,<sup>30</sup> there are few reported cases. In *People v. Palmer*,<sup>31</sup> expert testimony identifying gunshot particles based on SEM was upheld. According to the court, the technique has been generally accepted by the scientific community.<sup>32</sup>

#### Trace Metal Detection Technique

The trace metal detection technique (TMDT) is designed to determine whether a person has recently handled a metallic object, including a firearm. In this respect, it differs from GSR tests that are designed to determine whether a person has recently *fired* a firearm.

In 1970, the Law Enforcement Assistance Administration (LEAA)sponsored research first described TMDT.<sup>33</sup> This research showed that metal objects leave traces (metallic ions) when they come in contact with skin and clothing surfaces. When sprayed with a reagent and exposed to ultraviolet light, the metal traces can be detected by their fluorescent colors. In addition, characteristic patterns, such as those left by the handling of a firearm, sometimes can be identified:

<sup>30</sup> See Andrasko & Maehly, "Detection of Gunshot Residues on Hands by Scanning Electron Microscopy," 22 J. Forensic Sci. 279 (1977); Basu, "Formation of Gunshot Residues," 27 J. Forensic Sci. 72 (1982); Germani, "Evaluation of Instrumental Parameters for Automated Scanning Electron Microscopy/Gunshot Residue Particle Analysis," 36 J. Forensic Sci. 331 (1991).

<sup>31</sup> 80 Cal. App. 3d 239, 145 Cal. Rptr. 466 (1978).

<sup>32</sup> *Id.* at 252–254, 145 Cal. Rptr. at 472–473.

Examination by ultraviolet light of the metal trace patterns which appear as fluorescent colors on the hands or clothing of the suspect allows a police officer to determine whether a suspect has been in contact with certain metal objects, the type of metal or metals in the objects; and also to infer what type of weapon or metal object was probably involved.<sup>34</sup>

In sum, the color of the pattern provides information about the identity of the metal, and the location, size, and shape of the pattern provides information about the type of object that the test surface came in contact with. The research indicates that metal traces may be detected up to thirtysix to forty-eight hours after contact with a firearm, even if normal routine washings have occurred.

Further research disclosed that TMDT is not as straightforward a procedure as the initial LEAA publication had suggested, that the amenability of subjects to the test varied, and that the test 'involves highly subjective judgments.''<sup>35</sup> Thus, the successful use of the technique ''hinges upon the acquisition of considerable personal experience, augmented by the accumulation of an extensive photographic file of patterns characteristic of as many different weapons and tools as possible.''<sup>36</sup>

Of the few courts that have considered the admissibility of TMDT evi-

<sup>35</sup> Stevens & Messler, "Trace Metal Detection Technique (TMDT)," in *Practising Law Institute, Scientific and Expert Evidence* 1075, 1088 (2d ed. 1981).

<sup>36</sup> Stevens & Messler, "The Trace Metal Detection Technique (TMDT): A Report Outlining a Procedure for Photographing Results in Color, and Some Factors Influencing the Results in Controlled Laboratory Tests," 19 J. Forensic Sci. 496, 497 (1974).

<sup>&</sup>lt;sup>33</sup> National Institute of Law Enforcement & Criminal Justice, *Trace Metal Detection Technique in Law Enforcement* (Oct. 1970).

<sup>&</sup>lt;sup>34</sup> *Id*. at 1.

dence, most have admitted the evidence.<sup>37</sup> One court, however, has ruled TMDT evidence inadmissible for lack of general acceptance by the scientific community.<sup>38</sup> In addition, the state's failure to use TMDT, upon a defense request, has been held to violate due process.<sup>39</sup>

<sup>37</sup> See Reid v. State, 267 Ind. 555, 558–560, 372 N.E.2d 1149, 1151–1152 (1978); State v. Synder, 190 N.J. Super. 626, 631–633, 464 A.2d 1209, 1211– 1212 (1983); State v. Daniels, 37 Ohio App. 2d 4, 5–6, 305 N.E.2d 497, 498 (1973); Brotherton v. State, 666 S.W.2d 126, 129–130 (Tex. Ct. App. 1983).

<sup>38</sup> People v. Lauro, 91 Misc. 2d 706, 712–713, 398 N.Y.S.2d 503, 507 (Sup. Ct. 1977). See also Esquivel v. State, 595 S.W.2d 516, 528–529 (Tex. Crim. App.) (second TMDT test not admitted because it was not conducted under similar conditions as first test), *cert. denied*, 449 U.S. 986 (1980).

<sup>39</sup> People ex rel. Gallagher v. District

A striking aspect of the TMDT cases has been the lack of scientific testimony regarding the technique. In one case, the technician who administered the test and testified at trial "admitted that he had no understanding of the reason for the reaction that occurred when [the] test was administered."40 In another case, the expert admitted on cross-examination that he "had 'no idea' of the scientific community's acceptance of the trace metal test, he was unaware of any statistics supporting the test's reliability and he had no knowledge of the chemical composition of the reagent spray used in the test."<sup>41</sup> Despite these admissions, the evidence was admitted in both cases.

Court, 656 P.2d 1287, 1290–1292 (Colo. 1983).

<sup>40</sup> Reid v. State, 267 Ind. 555, 559, 372 N.E.2d 1149, 1152 (1978).

<sup>41</sup> Brotherton v. State, 666 S.W.2d 126, 129 (Tex. Ct. App. 1983).