Detection of Gunpowder/Gunpowder Residues
A State-of-the-Art Review and Recommendations for Further Research

Charles R. Midkiff Jr., Forensic Chemist
Forensic Branch
National Laboratory Center
Bureau of Alcohol, Tobacco and Firearms
U. S. Treasury Department, Washington, D. C.

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I Purpose of the Review

The Committee on New Development and Research, ASCLD has identified a number of areas of physical evidence examination for review and recommendation of further work. This review, prepared in response to their request, covers Topic #4, Detection of Gunpowder/Gunpowder Residues. Current methodologies were evaluated to define problem areas and limitations of the major approaches to residue detection. Recommendations for further work and improved information transfer were made from the study.

II Value of the Test

The ability to detect and identify powder and primer residues is of significant value in the investigation of crimes involving firearms. The detection of firearms discharge residues on the hands, indicative of recent handling or discharge of a firearm, provides important evidence in the investigation of assaults, armed robberies, homicides and suicides. Estimation of muzzle to target distance is useful in many shooting cases. In some situations, it is desirable to know the time of firing of a weapon or to identify suspected bullet holes in clothing or other materials.

III Current State of the Art

Present methodology has a number of limitations which affect its use in the field and the laboratory. Many of the currently used techniques lack sensitivity or specificity and are limited in their application to a narrow range of sample
types. On the other hand, the more effective approaches are limited in use by cost and long analytical times. Improved techniques are required which will reliably and rapidly detect and identify powder and primer residues. These techniques should offer sensitivity and specificity and, if feasible, at a cost within the range of the average forensic laboratory.

The detection of gunpowder/powder residues involves two related objectives. The detection of partially burned gunpowder is normally sought in connection with muzzle-to-target determinations. It has, in addition, potential application in the examination of hand samples to show recent firearm discharge. The detection of gunpowder residues may be considered as referring to the detection of materials from components of the primer or bullet as deposited either on the shooter's hands or on a target surface. For the examination of hand samples, primer components such as barium, antimony and lead are normally determined. The detection of these components and bullet lead, also allows muzzle-to-target distances to be estimated at ranges of 10 feet or more, well beyond the useful range of gunpowder patterns alone. Primer components are also used for the identification of suspected bullet holes and, in conjunction with powder combustion products, have provided the basis for attempts to determine how recently a firearm or spent cartridge was discharged.

As is evident from the attached bibliography, considerable effort has been devoted worldwide to gunshot/gunpowder detection. Analytical methodologies ranging from simple chemical tests to spectroscopic methods to scanning electron microscopy
has been evaluated. At present, a variety of techniques are used, each with advantages and limitations (See Table 1). For screening purposes, some chemical tests are used. Selected samples are then analyzed by more sophisticated methods. Typically, a sample may be tested for the presence of lead with sodium rhodizonate and then examined for primer components by neutron activation analysis (NAA) or atomic absorption spectroscopy (AAS). Similarly, screening may be done for nitrites in partially burned gunpowder using diphenylamine; then examined for barium and antimony from the primer by NAA or AAS.

Alternatively, samples may be examined directly by NAA or AAS. The major difficulty with both these instrumental techniques is that they provide only indications and not conclusive identification of firearms discharge residue. In addition, neither technique is suitable when .22 rimfire ammunition is used because most brands do not contain both barium and antimony in the primer composition. The most serious limitations of NAA are cost, availability and lengthy analysis time; these restrict its use to only a few laboratories. AAS is much more widely used, and its use is rapidly increasing. Of the techniques presently available, the most reliable is the combination of scanning electron microscopy combined with energy dispersive x-ray analysis (SEM/EDX). A sample is examined under high magnification and preliminary identification of micron size residue particles of smokeless powder or primer material is made based upon their morphology. A primer residue particle is analyzed for the presence of lead, barium and antimony by energy dispersive x-ray. The SEM/EDX approach is applicable to residues even
from .22 rimfire weapons without barium and antimony containing primers. Under favorable circumstances, the SEM/EDX approach can provide conclusive identification of gunshot residues. The major limitations of SEM/EDX are high equipment cost and long analysis times.

As indicated, research and development in the detection and identification of gunshot residues has been extensive. Most of this work, however, has been of the limited scope, in-house type. Only a few projects involving meaningful allocation of funds and resources have been identified. NAA projects include work conducted from the early 1960's to 1970 at Gulf General Atomic under AEC and LEAA sponsorship (Contract No. AT(04-3)-167 Div. Isotopes Development USAEC and LEAA) and work at the National Bureau of Standards in 1974-75 (LEAA Project Authorization NBSIR75). Other funded projects have included the determination of firing time by Electron Paramagnetic Resonance (EPR) at EG&G Inc. (LEAA contract through NILECJ 1972) and the evaluation of SEM (FORSEM - New York State Police 663 New York State Office of Criminal Justice, 1974). The major research project in gunshot residues is presently being performed at Aerospace Corp. (Contract J-LEAA-025-73) which has included an overview of detection methods and suggestions of potential approaches. In addition, Aerospace has examined Photoluminescence as a low cost detection method. Presently under evaluation and development are SEM/EDX, GC-MS and TLC approaches. Of these both SEM/EDX and GC-MS are expensive but TLC offers potential for use in local laboratories because its cost is low and both equipment and familiarity with the technique are common.
IV Needs and Recommendations

Several areas for research and development aimed toward improved detection and identification of firearms discharge residues have been identified. These needs are in three major categories: improved detection of residues on the hands, sample contamination and conclusive identification.

Of first priority is the development of a system which will reliably detect and identify residues up to several hours after firing. Present approaches are not satisfactory with a live subject because much of the residue is lost soon after firing. In actual case situations, samples may not be collected until some time following the incident and residue detection frequency is lower than desirable. Test results may often then be "inconclusive" even when other evidence strongly indicates firing by the subject. The SEM/EDX approach based upon particulate identification has shown better results than other techniques with delayed sampling. This method, however, is slow in favorable cases and with delayed sampling takes even longer to locate suitable particles for analysis. This makes the technique even less attractive than otherwise for laboratories with large caseloads. Automation of the SEM/EDX analysis is possible and would ease the analytical time restrictions, albeit at increased initial cost. Another approach with potential is examination for the presence of organic components which may have greater persistence than primer particulates. Both GC-MS and TLC approaches could be used with TLC being attractive in cost and availability.
A second area of needed development is the proper analytical treatment of samples contaminated with blood, grease or other foreign material. Contaminated samples pose both analytical and interpretation difficulties. If samples are contaminated with blood, grease or dirt, two analytical problems are encountered, with NAA or AAS methodology: effective leaching of the sample and high instrumental backgrounds. With SEM/EDX methodology, similar problems may be encountered. Foreign material may coat the residue particulates and complicate morphological identification. During the EDX phase, high backgrounds may be contributed, making interpretation difficult. A similar problem exists in firing-distance determinations where blood contamination obscures visualization of the powder pattern. Sample ashing and chemical techniques have received some attention for the examination of contaminated samples but other approaches should be studied. Exposure to certain materials, either through occupation or activity, can result in elevated levels of elements such as barium and antimony on the hands. When hand samples from individuals exposed to these contaminants are examined, problems in interpretation of results are encountered. It cannot be determined, by either NAA or AAS, if the elements detected arise from occupational contamination or are indicative of gunshot residues. A number of occupations have been identified and correlated with elevated barium and antimony levels. Preliminary work at the National Bureau of Standards with one of these occupations, auto mechanics, has shown that barium and antimony levels on the hands during working hours are quite high. This work also
showed that following after work clean-up, levels of the two elements decreased significantly and approach average handblank levels. This may indicate that claims of occupational contamination may be unrealistic. Particulate examination by SEM/EDX can be of assistance in the discrimination of occupational contamination and firing residues but studies applicable to AAS and NAA are needed. In addition to occupational contamination, activity contamination i.e. exposure to materials not specifically related to occupation is of concern in the interpretation of GSR test results. A study is needed to identify any materials which resemble firearms residues, either morphologically or chemically.

The third major category of needed development is in providing conclusive identification of residues from firings of weapons of all types and calibers. As mentioned, .22 caliber rimfire cartridges often do not contain barium and antimony in the primer composition and tests based upon these are ineffective. Low success rates are also obtained with long guns. Techniques based upon powder components or added tags probably provide the best approaches to reliable detection when these weapons are used. In addition, the use of added tags can provide additional information for use in an investigation.

The concept of tagging of ammunition or primers to allow rapid detection and unequivocal identification of firearms discharge residues is not new. A preliminary study and feasibility demonstration was made nearly ten years ago. With the
emerging use of taggants in explosives and inks, some consideration should again
be given to ammunition tagging. With properly selected tags not only could gun-
shot residues be detected, but manufacturers and calibers of factory loaded
ammunition could be identified as well. For handloaded ammunition, powder and/or
primers could be tagged to identify manufacturer and to designate the product as
being sold for handloading purposes. Initially an evaluation of candidate tagging
systems should be made. This would be followed by small batch testing and tag
recovery demonstrations. It has been claimed that because of high existing
inventories of ammunition, it would be years before tagging would be effective.
This argument is not supported by production and sales figures. Ammunition, des­
pite inventories, must enjoy a rapid turnover. Considering the annual production
of ammunition for handguns alone, if turnover were low, the market would have
long ago been saturated. As no apparent saturation exists, and unlimited inventory
buildup is unreasonable, turnover of ammunition must be high. With high turnover
of inventories of ammunition, tagging should be effective in one year and improve
in effectiveness each succeeding year.

In any systems developed for gunpowder/gunpowder residues analysis, consideration
must be given to cost and complexity of the equipment required to insure their
utilization by smaller laboratories. In addition, analysis time is of crucial
importance to the laboratory with large caseloads.

Development costs for systems suitable to resolve the problems described is
not easily estimated since much of the work to date is preliminary.
Perhaps as important as new R & D, improved technology transfer is needed between the research laboratory and the working laboratory and between large and small establishments. At present, transfer of information and technology into and within the forensic community is, at best, poor and much room for improvement exists. Improved communication of existing and developing methodology will substantially improve the state-of-the-art in the detection of gunpowder/gunpowder residues.

Charles R. Midkiff
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<table>
<thead>
<tr>
<th>Technique</th>
<th>Specificity</th>
<th>Cost</th>
<th>Speed</th>
<th>Status</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>Chemical Tests</td>
<td>Poor</td>
<td>Very low</td>
<td>Fast</td>
<td>Limited use</td>
<td>Used for both powder and primer residues</td>
</tr>
<tr>
<td>AAS</td>
<td>Good</td>
<td>Moderate ($15,000)</td>
<td>Fast</td>
<td>Wide usage</td>
<td>Good for primer residues, lead and copper</td>
</tr>
<tr>
<td>NAA</td>
<td>Good</td>
<td>Very high</td>
<td>Slow</td>
<td>Very limited usage</td>
<td>Good for primer residues, not lead</td>
</tr>
<tr>
<td>SEM/EDX</td>
<td>Excellent</td>
<td>High ($50,000)</td>
<td>Slow</td>
<td>Limited use</td>
<td>Under development</td>
</tr>
<tr>
<td>Photoluminescence</td>
<td>Good</td>
<td>Low</td>
<td>Fast</td>
<td>No present use known</td>
<td>Good for lead and antimony only</td>
</tr>
<tr>
<td>TLC</td>
<td>Unknown</td>
<td>Very low</td>
<td>Probably fast</td>
<td>None at present</td>
<td>Under evaluation and development</td>
</tr>
<tr>
<td>Electrometric Methods</td>
<td>Good</td>
<td>Low</td>
<td>Fast</td>
<td>Unknown</td>
<td>Initial evaluation and development only</td>
</tr>
<tr>
<td>Spectrometric Methods (Misc)</td>
<td>Good</td>
<td>Variable</td>
<td>Fast</td>
<td>Limited use</td>
<td>Rarely Used</td>
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</tbody>
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Charles R. Midkiff Jr.
Forensic Branch
National Laboratory Center
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Washington, D.C.

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