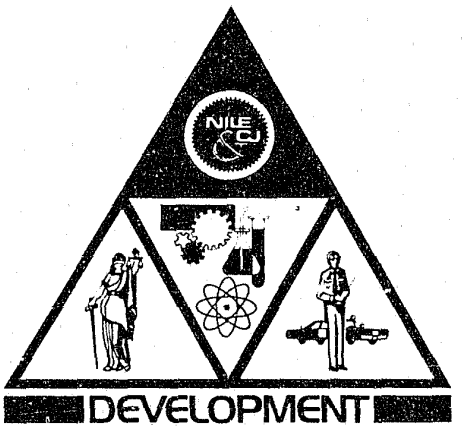
AEROSPACE REPORT NO.
ATR-77(7915)-2

EQUIPMENT SYSTEMS IMPROVEMENT PROGRAM

A FIELD TEST OF PHOTOLUMINESCENCE FOR INVESTIGATING SUICIDES BY FIREARMS

Law Enforcement Development Group

February 1978



Prepared for

National Institute of Law Enforcement and Criminal Justice
LAW ENFORCEMENT ASSISTANCE ADMINISTRATION
U.S. DEPARTMENT OF JUSTICE

The Aerospace Corporation

Aerospace Report No.
ATR-77(7915)-2

EQUIPMENT SYSTEMS IMPROVEMENT PROGRAM

A FIELD TEST OF PHOTOLUMINESCENCE FOR INVESTIGATING SUICIDES BY FIREARMS

Prepared by

G. L. Loper, A. R. Calloway, M. A. O'Neill,
S. A. Peak, G. M. Wolten, and P. F. Jones

Chemistry and Physics Laboratory
THE IVAN A. GETTING LABORATORIES
THE AEROSPACE CORPORATION
El Segundo, CA 90245

February 1978

LAW ENFORCEMENT DEVELOPMENT GROUP
THE AEROSPACE CORPORATION
Washington, D.C. 20024

Prepared for

National Institute of Law Enforcement
and Criminal Justice
LAW ENFORCEMENT ASSISTANCE ADMINISTRATION
U.S. DEPARTMENT OF JUSTICE

Contract No. J-LEAA-025-73

This project was supported by Contract Number J-LEAA-025-73 awarded by the National Institute of Law Enforcement and Criminal Justice, Law Enforcement Assistance Administration, U.S. Department of Justice, under the Omnibus Crime Control and Safe Streets Act of 1968, as amended. Points of view or opinions stated in this document are those of the authors and do not necessarily represent the official position or policies of the U.S. Department of Justice.

Aerospace Report No.
ATR-77(7915)-2

A FIELD TEST OF PHOTOLUMINESCENCE FOR INVESTIGATING SUICIDES BY FIREARMS

Approved

S. Siegel, Director
Chemistry and Physics Laboratory

J. Meltzer, General Manager
Law Enforcement and Telecommunications Division

ABSTRACT

This report describes the results obtained during a field test of a previously developed photoluminescence technique to detect lead and antimony (cartridge constituents) on the hands of a person who has recently fired a gun. The primary objective of this study was to evaluate the utility of this gunshot residue detection technique in the investigation of apparent gunshot suicides. This objective included the identification of any potential problems that might limit the application of this technique to suicide investigations. The field test was carried out by The Aerospace Corporation in conjunction with medical examiners and/or criminalistics laboratories in Los Angeles, Phoenix, Dallas, Atlanta, and Baltimore. Photoluminescence analyses were performed on handsamples collected by an adhesive lift sampling method from the backs of the hands of 67 apparent gunshot suicide victims, 41 coroner control subjects who had died of non-gunshot related causes, and 31 live occupational control subjects while they were engaged in work expected to result in high exposure to lead and antimony.

On the basis of the data obtained for the coroner and occupational control subjects, tentative simultaneous photoluminescence threshold levels of 0.85 μg for lead and 0.01 μg for antimony were selected as a conservative criterion for presuming that gunshot residue was present on the handsamples collected from the backs of hands of apparent gunshot suicide victims.

During the field test, the presence of blood on handsamples was found to have an adverse effect on the detectability of lead and antimony by the photoluminescence technique. This problem must be overcome before the photoluminescence method can achieve its full potential and be established as a field method for the investigation of gunshot suicides. Even with the unfavorable effect of blood on the analyses, 48 percent of the suicide cases involving all handguns other than .22-revolvers yielded detectable amounts of gunshot residue based on the simultaneous 0.85 μg lead and 0.01 μg antimony threshold levels. It is believed that the success rate for cases involving these guns would increase significantly in the absence of blood effects. Possible

methods are suggested for eliminating the adverse effects of blood on photoluminescence analyses. For cases involving .22-revolvers, rifles, and shotguns, a much lower success rate was obtained. This lower success rate is consistent with the sparse amounts of gunshot residue detected by other bulk elemental analysis techniques on handsamples collected during test firings of these guns.

This report also includes new information that compares background levels of lead on both hands of people who have not recently fired a gun. This information should be useful to the criminalistics laboratories which consider the ratio of the amounts of the elements characteristic of gunshot residue on one hand to that on the other hand as well as their absolute amounts in deciding whether a person has recently fired a gun.

From the data obtained in the field test, the foregoing simultaneous thresholds of 0.85 μg Pb and 0.01 μg Sb appear appropriate enough to permit distinguishing gunshot residue from handblank levels of these elements using the photoluminescence analysis technique with the adhesive lift collection method. However, the handblank data are limited in number, and these tentative threshold levels must still be confirmed or appropriately modified by additional data before valid comparisons can be made of the relative success rates of photoluminescence versus other bulk elemental analysis methods. The photoluminescence/adhesive lift technique will be at least as useful in gunshot suicide investigations if these threshold levels are confirmed.

CONTENTS

CONTENTS (Continued)

CONTENTS (Continued)

TABLES

FIGURES

ACKNOWLEDGMENTS

The authors express their gratitude to the personnel at the following offices for their contributions to this study:

Chief Medical Examiner/Coroner, County of Los Angeles, California
Maricopa County Medical Examiner, Phoenix, Arizona
Southwestern Institute of Forensic Science, Dallas, Texas
Georgia State Crime Laboratory, Atlanta, Georgia
Chief Medical Examiner, Baltimore, Maryland
Scientific Investigation Bureau of the Nassau County, New York, Police Department

The support and encouragement of the National Institute of Law Enforcement and Criminal Justice is gratefully acknowledged, with special thanks to J. Kochanski, G. Schollenberger, L. Shubin, and J. Sullivan.

SUMMARY

The first objective of the field test study reported in this document was to obtain data to evaluate the use of a photoluminescence analysis technique in the investigation of apparent gunshot suicides. This objective included the identification of any potential problems that might limit the application of this technique to these investigations. The second objective was to use the photoluminescence technique to obtain additional data which concerned the levels of lead and antimony on the hands due to environmental or occupational exposure. A third and subsidiary objective was to determine the frequency with which smokeless powder fragments are found on the hands of suicide victims. The photoluminescence technique, which detects lead and antimony in gunshot residue, had been previously developed in part under a contract with the Law Enforcement Assistance Administration (LEAA). The field test study was conducted at medical examiners and/or criminalistics laboratories which represent five different geographical regions of the United States. During the study, the photoluminescence technique was used to quantitatively determine the amounts of lead and antimony on the backs of the hands of 67 gunshot suicide victims in comparison to the amounts of these elements on the backs of the hands of control subjects. Two groups of control subjects were studied. One group included 41 coroner control subjects. These were persons who had died of causes other than gunshot wounds. The other control group included 31 live subjects who were members of certain occupational groups expected to have high exposure to lead and antimony.

The amounts of lead and antimony found on the backs of the hands of the coroner control subjects are expected to be similar to the amounts of these elements found on the backs of the hands of members of the general population sampled at random. Information concerning these handblank levels is required to distinguish firing from nonfiring handsamples. None of the coroner control subjects were found to have handsample levels of lead and antimony that were simultaneously above 0.85 μg and 0.01 μg, respectively. The levels of lead and antimony found on the backs of the hands of the occupational control subjects are expected to be much higher than the levels of these elements on persons selected at random from the general population. Slightly less than

10 percent of these control subjects were found to have handsample levels of lead and antimony that were simultaneously above 0.85 μg and 0.01 μg, respectively. On the basis of these limited handblank data, simultaneous threshold levels of 0.85 μg for lead and 0.01 μg for antimony were tentatively selected as the minimum levels of these elements necessary before the presence of gunshot residue on handsamples could be presumed. Gunshot suicide cases with handsample analyses above these simultaneous threshold levels were concluded to be correctly identified as having gunshot residue present. The handblank data are limited. Therefore, these tentative thresholds must be either confirmed or appropriately modified by additional data before the success rate of the photoluminescence method can be compared to that of other bulk elemental analysis methods. The photoluminescence/adhesive lift technique will be at least as useful in gunshot suicide investigations if these simultaneous threshold levels are confirmed.

A problem relating to the establishment of the photoluminescence technique for field use was uncovered during this study. The presence of blood on handsamples was found to have a deleterious effect on the detectability of lead and antimony. Approximately 50 percent of the gunshot suicide cases studied during the field test were observed to have blood on at least one handsample after collection. Even with the adverse effect of blood on the photoluminescence analyses, 48 percent of the suicide cases involving all handguns other than .22-revolvers were concluded to be correctly identified as having gunshot residue present on at least one handsample after collection. This represents a lower limit success rate that would be expected to increase significantly if the unfavorable blood effects on the photoluminescence analyses could be overcome. A much lower success rate was obtained for cases involving .22-revolvers, rifles, and shotguns. The low success rate obtained for long gun and .22-revolver cases is expected, however, on the basis of the sparse amounts of gunshot residue found by other bulk elemental analysis techniques on handsamples taken during test firings of these guns.

The presence of blood on handsamples is also a source of difficulty in atomic absorption analysis of gunshot residue. Particulate matter produced from the blood during analysis may cause interferences due to scattered light. Incomplete sample leaching prior to analysis may also occur. As a result of the adverse effects of blood on both techniques, the photoluminescence technique and the atomic absorption technique would be expected to be roughly equivalent in their applicability to gunshot suicide investigations. The harmful effects of blood on atomic absorption analyses can be overcome by the use of a low pressure oxygen plasma ashing technique.

The limited time available in the field test did not allow for the development of procedures to overcome blood effects on photoluminescence analyses. Methods that may be used to remove blood from handsamples prior to photoluminescence analysis include either the low pressure oxygen plasma ashing technique used prior to atomic absorption analyses, or oxidation with chemical agents such as hydrogen peroxide. It is expected that the use of either of these oxidative processes would require chemical reduction of the lead or antimony ions back to their respective +2 and +3 oxidation states prior to photoluminescence analyses. It is likely that the photoluminescence technique of gunshot residue detection would be quite useful to suicide investigations if the harmful effects of blood on these analyses can be overcome.

CHAPTER I. INTRODUCTION

Since March of 1974, The Aerospace Corporation has been under contract to the National Institute of Law Enforcement and Criminal Justice, the research branch of the Law Enforcement Assistance Administration, to develop improved methods for detecting gunshot residue on the hands of a person who has recently fired a gun. A survey and technical assessment[1] of the techniques used by criminalistics laboratories to detect gunshot residue was completed in 1974, and possible alternative approaches to more reliable tests for its detection were identified.

As a result of recommendations made in the foregoing survey and assessment report, The Aerospace Corporation has investigated the feasibility of three potential approaches to improved gunshot residue detection and identification. The first approach involves the use of a photoluminescence technique for detecting gunshot residue. Using this technique, which is described in two previously published documents,[2,3] quantitative elemental analyses are carried out to detect lead and antimony in residue from the hands of an individual suspected of having fired a handgun.

This report describes the results of a five-month effort in which medical examiners and/or criminalistics laboratories in Los Angeles, Phoenix, Dallas, Atlanta, and Baltimore participated with The Aerospace Corporation in a field test of the photoluminescence technique to detect gunshot residue. The photoluminescence technique, which is described in this report, was used to determine the amounts of lead and antimony in residue from the hands of gunshot suicide victims in comparison with the amounts of these elements detected in residue from the hands of persons who had died of other causes.

The second method, described in a separate report,[4] is based on the observation that discrete micrometer-sized particles from the primer and bullet are deposited on the firing hand of an individual who discharges a handgun. This method involves the use of a scanning electron microscope (SEM) in conjunction with energy-dispersive x-ray analysis to identify gunshot residue particles by combining information about the morphology of individual particles with their elemental content. Detailed characterization studies, which were carried out during the past year and a half, indicate that gunshot residue particles have a characteristic size range,

morphology, and elemental content (lead, barium, and antimony, among others), which by SEM analysis allows them to be readily distinguished in most cases from particles of occupational or environmental origins. However, due to the high cost and complexity of the SEM, this method is more suitable for large well-equipped criminalistics laboratories than for the smaller laboratories.

For the third approach, it was thought that it might be possible to detect organic compounds which are characteristic of smokeless powder or its combustion products on the hands of a person who had recently fired a handgun. The work that was accomplished to determine the validity of this concept is described in another separate report.[5] The results of this study indicate that this type of test is possible when intact or partially burned flakes of smokeless powder can be recovered. In these situations, it was demonstrated that a simple confirmatory test for smokeless powder could be performed by thin-layer chromatography (see Appendix D). However, within the detection limits of the gas chromatography-mass spectrometry methods used in the exploratory phase of this work, there was no indication of the presence of any recoverable amounts of organic constituents characteristic of gunshot residue in the form of a dust or film on the hand following the firing of a handgun.

The photoluminescence technique for the detection of gunshot residue used in the field test reported in this document is based on the fact that various amounts of lead and antimony are often deposited on the hand from the bullet and primer upon the firing of a handgun. For this method to be useful, the amounts of lead and antimony found must be shown to exceed environmental background levels; occupational exposure to these elements must also be ruled out independently. The development of this technique was initiated in 1973 at The Aerospace Corporation under a company-financed research program in forensic science. Further development was subsequently incorporated into the work accomplished under contract to the Law Enforcement Assistance Administration. In terms of cost and ease of analysis, this technique offers advantages over the bulk elemental analysis detection procedures of neutron activation analysis and atomic absorption spectroscopy.

The objectives of the field test study were to obtain data to: (1) allow evaluations to be made of the use of the photoluminescence technique in particular and other elemental analysis procedures in general in the investigations of apparent gunshot suicides, (2) obtain additional information concerning the levels of lead and antimony on hands due to environmental or occupational exposure, and (3) determine how often fragments of powder are observed on the hands of suicide victims.

In Chapter II of this report, the photoluminescence technique for the detection of gunshot residue is compared with other bulk elemental analysis gunshot residue detection methods, and the rationale for the field test is described. Chapter III includes descriptions of the photoluminescence technique and the procedures used in the field test. The data obtained in the field test are presented in Chapter IV, along with a discussion of the field test results. Chapter V contains the conclusions which have resulted from the field test.

CHAPTER II. BACKGROUND AND RATIONALE FOR FIELD TEST

A variety of chemical color tests have been used over the past forty years in an attempt to detect residues of nitrates and nitrites as combustion products from smokeless gun powder,[6] and to detect the residues of antimony, barium, or lead from the primer or bullet.[7] These color tests generally have been found to be of questionable reliability due to the lack of either sufficient specificity or sensitivity.

When the gunshot residue detection Survey and Assessment Report[1] was completed by The Aerospace Corporation in 1974, the most widely accepted method for gunshot residue detection was neutron activation analysis for antimony and barium residues derived from the primer.[8] However, flameless atomic absorption spectroscopy could be used to detect not only antimony and barium in gunshot residue, but also lead.[9] It was beginning to replace neutron activation analysis as the preferred technique to detect gunshot residue.

The neutron activation analysis procedure lacked sufficient sensitivity to detect lead in gunshot residue, and required turnaround times of a month or more because samples had to be sent to a nuclear reactor facility for analysis. As usually practiced, gunshot residue detection procedures based on neutron activation analysis also had the disadvantage of requiring time-consuming radiochemical separation steps.

Laboratories that could afford the $10,000 to $18,500 cost of the instrumentation that was needed to apply flameless atomic absorption spectroscopy to gunshot residue detection could obtain results on a local basis more promptly and conveniently by this technique than by sending samples to a central laboratory for neutron activation analysis. One slight inconvenience in the use of atomic absorption spectroscopy for gunshot residue detection is that lead, barium, and antimony cannot be simultaneously analyzed with commercially available equipment, but must be determined sequentially, using separate samples.

The Aerospace-developed photoluminescence technique for the detection of lead and antimony in gunshot residue can be carried out more cheaply and simply than the atomic absorption technique for gunshot residue detection. Complete spectrofluorometers of the type used by the laboratories participating in the field test described in this report are commercially available at a cost approximately one-half that of the instrumentation required for flameless atomic absorption spectroscopy. Photoluminescence instrumentation capable of detecting both lead and antimony in gunshot residue (see Chapter III) can be easily assembled from commercially available components for approximately $3,500, while a filter fluorometer with sufficient sensitivity to detect only antimony in gunshot residue can be assembled for less than $1,500.

Valuable information concerning the levels of antimony, barium, and lead which are to be expected on the hands of persons who have and have not fired a gun has been obtained through the use of the bulk elemental analysis procedures of neutron activation analysis,[8] atomic absorption spectroscopy,[9] and photoluminescence.[2,3] However, the detection of these elements on the hand(s) of a person does not in itself provide conclusive identification of gunshot residue. Lead and barium are common in the environment and can be found in varying amounts on the hands of most people. Antimony is less common and is usually detectable only on the hands of individuals employed in special occupations such as automobile mechanics, electronic assemblers, machinists, and painters,[8] and also as lead smelter employees.[4]

To confirm the presence of gunshot residue, it is necessary to show that the amounts of these elements on the hand(s) exceed the levels that could be expected to result from occupational or environmental exposure. This problem is further compounded by the fact that gunshot residue on the hands of a normally active person declines rapidly with time, and decreases generally by an order of magnitude from its initial value in one hour after a gun is fired.[3,4]

In order to account for environmental sources of barium and antimony, the Bureau of Alcohol, Tobacco, and Firearms (ATF) has suggested

threshold values of 0.3 and 0.2 μg for these elements, respectively. Except for high levels due to occupational exposure, it was recommended that only amounts greater than these values should be taken to represent evidence for the presence of gunshot residue. However, a study conducted by Gulf General Atomic Corporation,[8] has shown that even in hand samples taken immediately after outdoor test firings, the recommended ATF threshold value of 0.3 μg for barium was exceeded in only about 55 percent of the firings of .38 and .22 caliber handguns, while the threshold value of 0.2 μg for antimony was exceeded in only about 50 percent of the .38 caliber firings and in 10 percent of the .22 caliber firings.

For an immobile subject such as a gunshot suicide victim, the rapid loss of residue from the hands with time is not experienced if the victim's hands are not disturbed. The success rate of bulk elemental analysis techniques for gunshot suicide investigations should depend primarily upon the quantity of residue deposited by the ammunition used, and should be less dependent on the time that has elapsed between the firing and sampling. In these cases, where the primary objective is the confirmation of the authenticity of a questioned suicide rather than obtaining evidence for a conviction, elemental analysis techniques may, as a minimum, be adequate for screening procedures for gunshot residue detection. The atomic absorption and photoluminescence elemental techniques are less costly and time-consuming than particle analysis.

Intact or partially burned flakes of smokeless powder can sometimes also be observed on the firing hand of a person who has discharged a handgun if the hand is examined promptly or if the person remains immobile. Confirmation of the nature of these flakes can be accomplished by thin layer chromatography. By this method, residue can be readily and inexpensively shown to be of smokeless powder origin by the identification of the characteristic organic compounds, nitrocellulose or nitroglycerine. Smokeless powder flakes are lost so rapidly from the hands through normal activity that their identification on the hands of living subjects is seldom of practical

criminalistic value; however, smokeless powder flakes may be helpful in apparent suicide investigations. More information is needed before it can be determined whether or not these flakes can be observed frequently enough in suicide cases to merit the time and effort spent in identifying them.

To determine how useful both photoluminescence analysis and the identification of organic flakes would be in gunshot suicide investigations, the laboratory personnel that participated in the field test were requested to conduct the following tasks over a four-month period from mid-February 1977 to mid-June 1977:

- carry out the photoluminescence determination of the quantity of lead and antimony on the hands of gunshot suicide victims and also on the hands of a number of controls (people who had died of causes other than gunshot), and
- as a subsidiary task, visually examine the hands of gunshot suicide victims for the presence of organic powder flakes and tabulate the frequency and quantity of their occurrence for statistical purposes.

The personnel of the participating laboratories were asked to record as complete a description as possible of the gun and cartridge used, along with other circumstances for each suicide (see Appendix A). The laboratories and personnel that collected handsamples and/or performed analyses during the field test reported in this document are listed in the first six entries of Table 1. The last entry is the Scientific Investigation Bureau of the Nassau County Police Department, which has initiated a two-year program to examine the usefulness of the photoluminescence technique for the detection of gunshot residue on the hands of gunshot suicide victims.

Table 1. Field Test Laboratory and Personnel Participants

Laboratory	Participating Personnel
Georgia State Crime Laboratory Atlanta, Georgia Director: Larry B. Howard, PhD	Warren Tillman Kenneth Czyscinski, PhD
Medical Examiner's Office Fulton County, Georgia Director: Robert R. Steivers, MD	Robert R. Steivers, MD Sgt. J. T. Cameron
Office of the Chief Medical Examiner State of Maryland Department of Post-mortem Baltimore, Maryland Director: Russell S. Fisher, MD, Chief	Bert Morton, MD, Deputy Chief Yale Caplan, PhD
Southwestern Institute of Forensic Sciences Dallas, Texas Director: Charles Petty, PhD	Irving C. Stone, PhD Larry Fletcher
Department of the Chief Medical Examiner/Coroner Los Angeles, California Director: Thomas T. Noguchi, MD, Chief	Marc Taylor Tuan Nguyen
Maricopa County Medical Examiner's Office Phoenix, Arizona Director: Ramon A. Morano	Ramon A. Morano Marilyn Elsmore
Scientific Investigation Bureau Nassau County Police Department Mineola, New York Laboratory Director: Capt. Henry Hack	Det. Thomas A. Kubic Det. Henry T. Galgan

CHAPTER III. FIELD TEST PROCEDURES

A. Detection of Lead and Antimony by Photoluminescence

Photoluminescence can be described as the light emitted by a molecular species in the ultraviolet-visible region (~265 nm to 700 nm) of the electromagnetic spectrum upon the absorption of exciting light of shorter wavelengths (190 nm to 380 nm).

The photoluminescence technique for the quantitative detection of lead and antimony in gunshot residue[2,3] is based on the strong luminescence observed at low temperatures for halogen ion complexes of certain metals[10,11] having the electronic shell configuration $1s^2 \ldots\ldots np^6\ nd^{10}\ (n+1)\ s^2$. The transition responsible for this luminescence is believed to be analogous to the intense $^3P_1 \rightarrow {}^1S_o$ emission observed for mercury atoms at 253.7 nm.

Strong luminescence is thus observed at low temperatures for sub-microgram amounts of the chloride and bromide ion complexes of the mercury-like ions gallium (I), germanium (II), arsenic (III), selenium (IV), indium (I), tin (II), antimony (III), tellurium (IV), thallium (I), lead (II), and bismuth (III). No luminescence can be observed from halogen ion complexes of 45 other inorganic ions under the same experimental conditions.[11]

Low temperature complexing of lead (II) and antimony (III) by the chloride ion in concentrated hydrochloric acid solutions provides the most sensitive, convenient, and rapid method for luminescence analysis known for these metal ions. The capability for sequentially analyzing for both ions in the same sample is also provided.

The luminescence quantum yields (the fractions of initially excited molecules that eventually luminesce) of lead (II) and antimony (III) chloride ion complexes are much larger at the 77 K boiling point of liquid nitrogen than at room temperature.

Concentrated HCl solutions (~6M to 8M) form transparent glasses at 77 K. Photoluminescence measurements of samples in concentrated HCl

solutions can thus be conducted in spectrofluorometers that employ the conventional 90-degree optical geometry between the incident radiation and the luminescence detector. This viewing geometry substantially reduces the experimental errors due to scattered light that arise with the frontal viewing geometry required for opaque samples.

Lead styphnate and antimony sulfide are both major constituents of most cartridge primers and form luminescent lead (II) and antimony (III) chloride ion complexes when dissolved in concentrated hydrochloric acid:

$$Pb^{+2} + 4Cl^- \longrightarrow PbCl_4^{-2}$$

$$Sb^{+3} + 4Cl^- \longrightarrow SbCl_4^-$$

$$Sb^{+3} + 6Cl^- \longrightarrow SbCl_6^{-3}$$

The lead (II) and antimony (III) chloride ion complexes may also be formed by dissolution of metallic lead and antimony from the bullet by concentrated HCl. Barium ion, from the primer constituents barium nitrate or barium peroxide, does not luminesce in frozen HCl solutions. At 77 K (see Figures 1 and 2), the emission spectrum (the plot of the variation in luminescence intensity at a fixed excitation wavelength as a function of emission wavelength) for the chloride ion complex of lead (II) exhibits a maximum at 390 nm, while the emission maximum for the chloride ion complex(es) of antimony (III) occur(s) at 620 nm. The emission maximum at 425 nm in Figure 2 is due to a combination of scattered light and HCl impurity emission. The excitation spectra (the plot of the luminescence intensity at a fixed emission wavelength as a function of excitation wavelength) can be observed to peak near 276 nm in Figure 1 for the chloride complex of lead (II), and at 250 nm and 300 nm in Figure 2 for the chloride complex(es) of antimony (III).

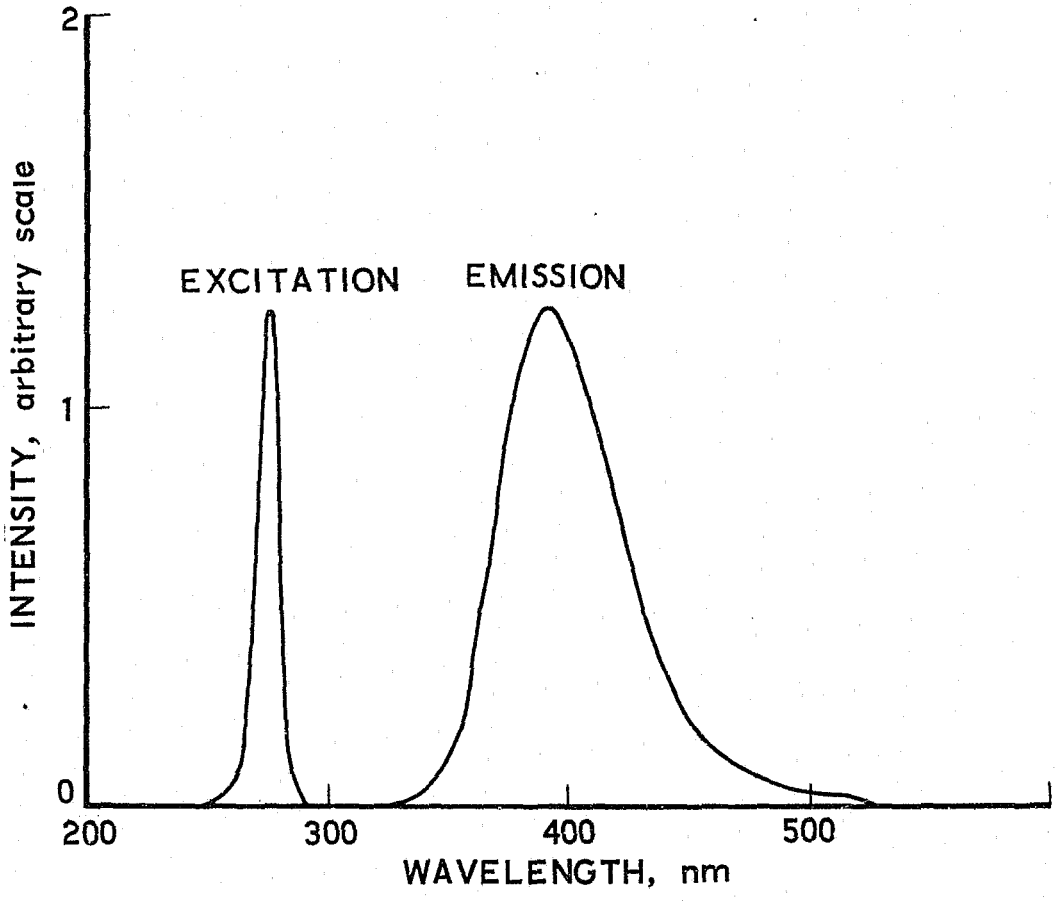
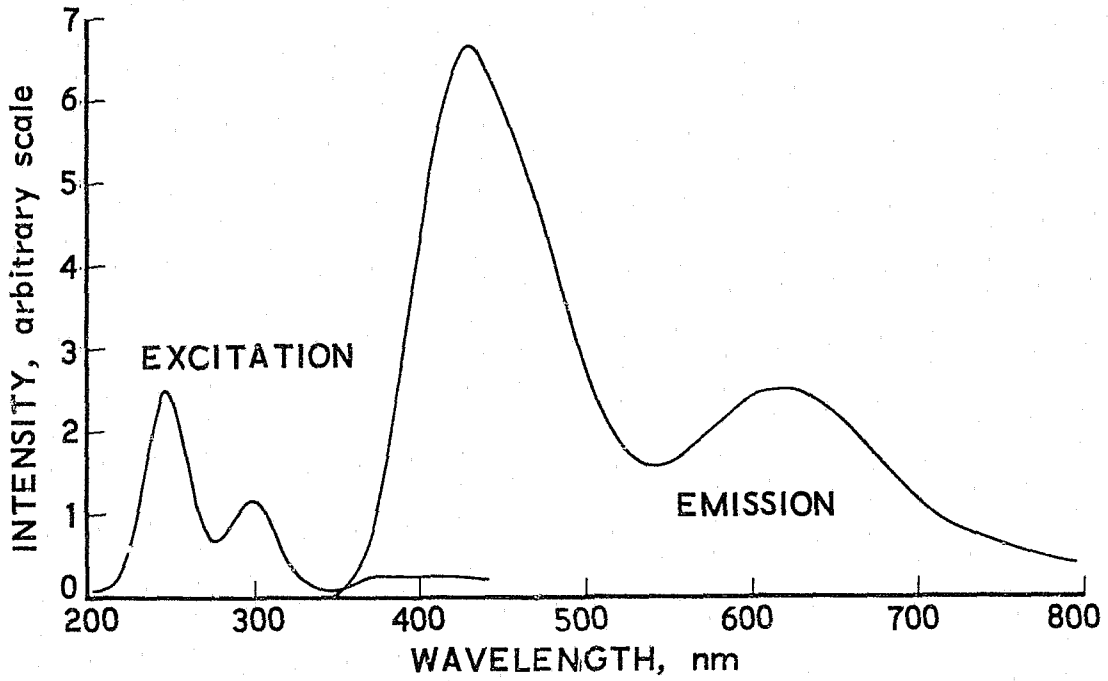


Figure 1. Excitation Spectrum (at 390-nm Emission) and Corrected Emission Spectrum (at 276-nm Excitation) for 1.0 μg/ml Pb (II) in 7 M HCl at 77 K



NOTE: The emission peak at 620 nm is the result of Sb, and the peak at 425 nm is a combination of scattered light and HCl impurity emission.

Figure 2. Excitation Spectrum (at 620-nm Emission) and Corrected Emission Spectrum (250-nm Excitation) for 0.20 μg/ml Sb (III) in 7 M HCl at 77 K

B. Equipment Required for Photoluminescence Detection of Lead and Antimony

The major item of equipment required for photoluminescence analysis is a fluorometer. The basic components of a fluorometer include an ultraviolet-visible light source, excitation and emission wavelength selectors, and a luminescence detector.[a] To conduct photoluminescence analysis on a sample, the excitation wavelength selector is set to allow only light in a certain wavelength region from the light source to be imaged on the sample. Luminescence from the sample is then focused through the emission wavelength selector, which is set to pass only wavelengths characteristic of the

[a]Refer to Figure 22 of Reference 1 for a block diagram of fluorometer components.

luminescence of the constituent to be measured. Light passing through the emission wavelength selector is then detected by the luminescence detector.

The fluorometer light source generally consists of either:

- a high-pressure xenon arc lamp that emits high-intensity continuum radiation (such that its spectral output varies smoothly with wavelength), or
- a low or medium pressure mercury vapor arc lamp that emits light efficiently only at several fixed wavelengths.

The excitation and emission wavelength selectors are usually either monochromators or optical filters, while a photomultiplier tube is used as the luminescence detector. Depending upon their spectral response characteristics, photomultiplier tubes are available for use in detecting low light levels from the ultraviolet to the near infrared region of the electromagnetic spectrum.

The photoluminescence instrumentation used in the field test described in this document included only spectrofluorometers, which are fluorometers equipped with xenon lamp excitation sources, and both scanning excitation and emission monochromators. Complete spectrofluorometers are available commercially from several manufacturers.[1] Alternatively, they can be easily assembled from modular components which can be purchased separately. These instruments are capable of determining both the excitation and emission spectra of a sample. The shape of the excitation and emission spectral profiles often provide a high degree of specificity to photoluminescence analysis.

An instrument capable of determining only excitation spectra could be used to detect lead and antimony in gunshot residue just as well as an instrument that is capable of determining both excitation and emission spectra. Such an excitation-only instrument can be assembled for approximately $3500 by using appropriate optical filters in front of the photomultiplier tube (instead of an emission monochromator) to isolate the wavelength regions in which the chloride ion complexes of lead (II) and antimony (III) exhibit emission maxima.

Filter fluorometers which use mercury vapor lamps as excitation sources are simpler and less expensive instruments. Optical filters are used both to:

- select one of the lines from the mercury vapor lamp as the excitation wavelength, and
- isolate the wavelength region in which emission is to be detected by the photomultiplier tube.

These instruments are not capable of providing excitation or emission spectra and would be expected to be much less specific towards detection of gunshot residue than instruments with xenon lamp excitation sources and scanning excitation monochromators. Limited results to date from hand-blanks and handsamples taken in test firings indicate that interfering signals from hand contaminants may not be an important problem in the photoluminescence analysis for antimony on live subjects.[3] This study also showed that a commercial filter fluorometer can be modified to provide the sensitivity to adequately detect antimony in gunshot residue. With the proper choice of excitation and emission filters and photomultiplier tube, it is conceivable that a filter fluorometer could be assembled for less than $1500, which could be used to adequately detect both lead and antimony in gunshot residue for screening purposes.

The laboratories that conducted photoluminescence analyses during the field test used their own spectrofluorometers, which included two different commercial models. The Maricopa County Medical Examiner's Office and the Georgia State Crime Laboratory used Perkin-Elmer Model MPF2A spectrofluorometers. The other laboratories, including The Aerospace Corporation, used Aminco-Bowman Model 4-8202 spectrofluorometers. The photomultiplier tubes (S-5 spectral response), which were provided as standard equipment with each of these instruments, lack sufficient red-sensitivity to adequately carry out the analysis of antimony in gunshot residue. To overcome this problem, a Hamamatsu R-777 photomultiplier tube (S-20 spectral response) was provided to each laboratory with the exception of the

Los Angeles County Medical Examiner's Office. The instrument in the latter laboratory had been previously equipped with a Hamamatsu R-446 photomultiplier tube (S-20 response). The Hamamatsu R-777 tube fits directly into the Perkin-Elmer spectrofluorometers. Aminco-Bowman J10-219 photomultiplier tube sockets are required to connect unpotted tubes such as the R-777 and R-446 to the photomultiplier microphotometers used in Aminco-Bowman spectrofluorometers.

Additional equipment which was provided to the laboratories that conducted the photoluminescence analyses included Suprasil quartz sample Dewars and sample tubes, outer Dewar collars, inner Dewar sample tube fittings, and optical cut-off emission filters (Schott FG-10). The laboratories which did not already have liquid nitrogen were reimbursed for the costs of the liquid nitrogen used in this project.

As originally equipped, none of the spectrofluorometers used in the field test had the manufacturer-supplied sample compartment accessories necessary to directly accept the sample Dewars needed to conduct the low temperature luminescence measurements. The Aerospace Corporation fabricated and provided special adapters for the sample compartment of each spectrofluorometer. The sample compartment of each Perkin-Elmer spectrofluorometer was modified to accommodate a sample Dewar by removing both the solution cell cuvette holder and the disk-shaped metal cover plate to the sample compartment. Each sample compartment cover plate was replaced by 1/8-inch thick disk of balsa wood of the same diameter from which a circular section had been removed that was just large enough to accept the outer collar designed to hold a sample Dewar.

For each Aminco-Bowman spectrofluorometer, the cuvette and slit holder assembly were removed along with the sample compartment cover plate. These were replaced by comparable parts fabricated from balsa wood (see Figure 3), which were designed to permit the sample compartment to accommodate a sample Dewar.

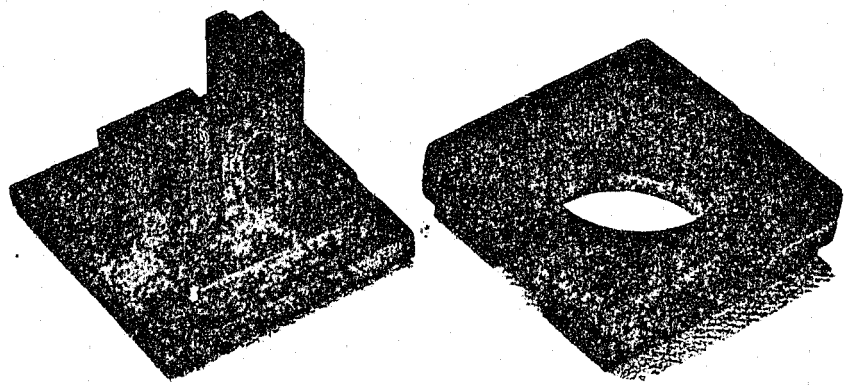


Figure 3. Fabricated Slit and Dewar Holder for the Aminco Spectrofluorometer

C. Handsampling and Photoluminescence Procedures, and Smokeless Powder Flake Analysis Procedures

Each laboratory that collected handsamples was provided with sampling disks and instructions in their use (see Appendix B). The sampling disks were identical to those used to collect handsamples for scanning electron microscope particle analysis. These disks were 2.5 cm in diameter and were made from either of two aluminum alloys (No. 6063 or 1100), which are low in the elements of interest in gunshot residue. The disks were coated on one side with Scotch No. 465 adhesive transfer tape. Generally, the backs of both hands of a subject were sampled separately. This involved sampling the web area between the thumb and forefinger, the backs of the fingers, and the back of the hand.

Prior to performing photoluminescence analyses, it was necessary that each laboratory construct calibration plots for detecting the chloride ion complexes of lead (II) and antimony (III) using their own spectrofluorometer. For each laboratory, this involved preparing plots of the luminescence intensity of the chloride ion complexes of lead (II) and antimony (III) versus various standard concentrations of lead (II) and antimony (III) in concentrated

hydrochloric acid. Analyses of handsamples were carried out by first accurately pipetting 0.5 ml of 7M HCl onto the surface of the sampling disk and allowing the HCl to soak and react for ~3 minutes, a Pasteur pipet was used to transfer it from the adhesive surface (Figure 4) to a Suprasil quartz-tipped sample tube of 4-mm inside diameter and 6-mm outside diameter. The sample tube containing the HCl-residue sample was then placed in a Suprasil quartz-tipped sample Dewar containing liquid nitrogen (Figure 5), and analyzed for lead and antimony content.

Quantitative lead and antimony analyses were accomplished by determining excitation spectra. For antimony analyses, the emission monochromator of the scanning spectrofluorometer was set at 660 nm and the excitation maxima of the antimony (III) chloride ion complex(es) were monitored at 250 nm and 300 nm. Emission was observed at 660 nm, rather than at 620 nm where the emission maximum occurs, in order to minimize background interference. A Schott FG-10 optical cut-off filter of low luminescence was placed between the sample compartment and the emission monochromator to prevent scattered excitation light from reaching the monochromator. For lead analyses, the emission monochromator was set at the emission maximum of the chloride ion complex of lead (II) (390 nm) and the excitation maximum was monitored at 276 nm. The use of an emission filter was not required for lead analysis.

Detailed descriptions of the procedures used to construct calibration plots for the chloride ion complexes of lead (II) and antimony (III) and for detecting lead and antimony in handsamples are presented in References 2 and 3, and also in Appendix C. These procedures were provided to each field test participant. Thin-layer chromatographic procedures for confirming the presence and identity of unburned or partially burned smokeless powder flakes on the hands of gunshot suicide victims were also provided to each field test participant for use in selected cases as desired. These procedures are contained in Appendix D.

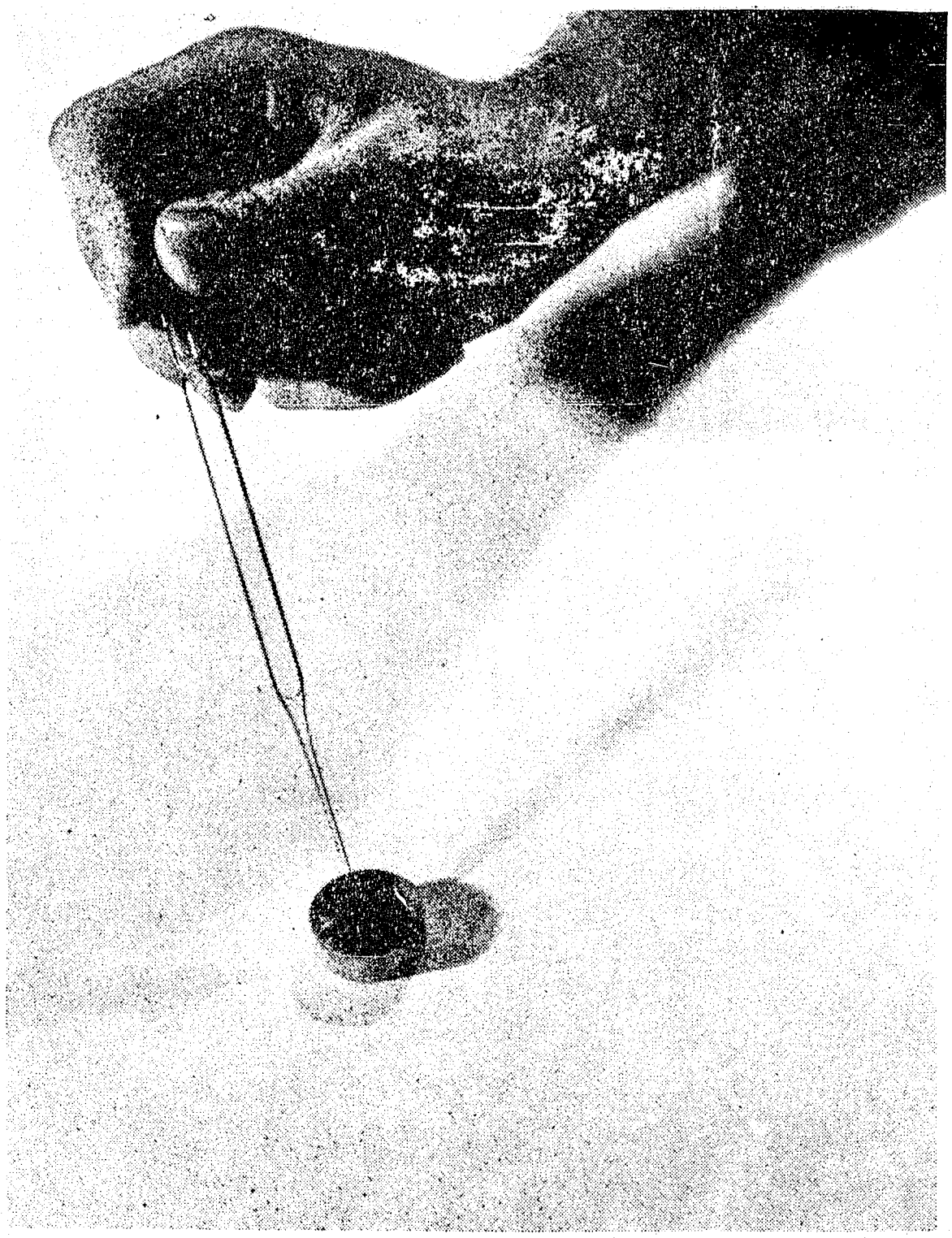


Figure 4. Pasteur Pipet and Handsampling Disk

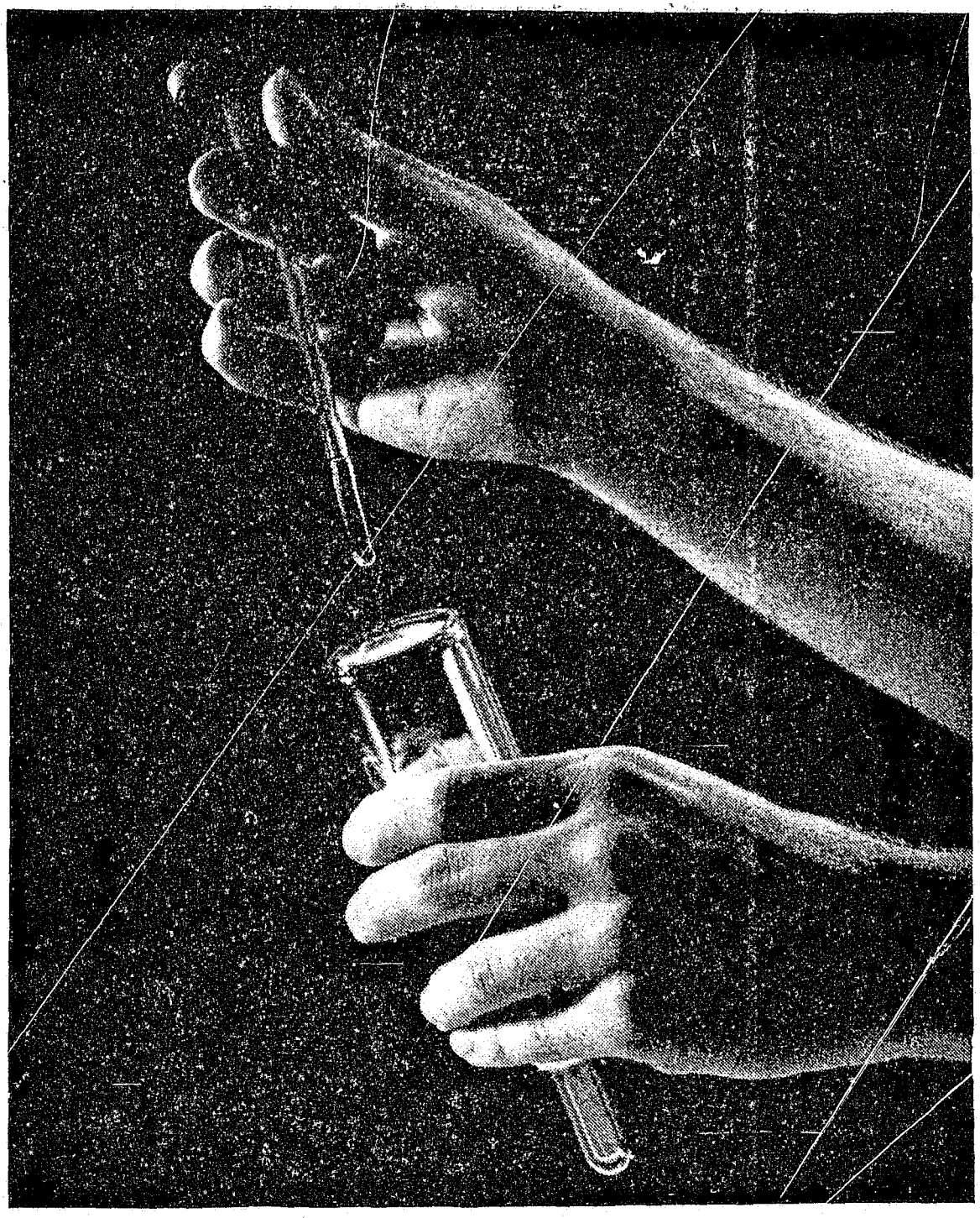


Figure 5. Quartz-Tipped Dewar Flask and Quartz Sample Tube Containing HCl Gunshot Residue Solution

CHAPTER IV. RESULTS AND DISCUSSION

The results of the bulk elemental analyses of handsamples from gunshot suicide victims by photoluminescence are presented in Appendix E. Also included are the results of analyses of control handsamples (handblanks) from subjects who died by causes other than gunshot wounds. The data in Appendix E are grouped by laboratory. Analyses of handsamples from gunshot suicide cases P-1 through P-12, D-1 through D-30, A-1 through A-11, B-1 through B-3, L-1 through L-15, and control cases LC-6 through LC-8 were carried out at the participating laboratories. Handsamples from the other gunshot suicide cases and control cases collected by these laboratories were analyzed at The Aerospace Corporation because of the limited time available for the field test and manpower restrictions at each laboratory.

The amounts of lead and antimony found on the hands of control subjects are discussed in Section A of this chapter. These results provide information on the levels of these elements expected on the hand due to environmental and occupational exposure. Section B compares the amounts of lead and antimony found on the hands of gunshot suicide victims with the amounts obtained in previous test firings. The effect of blood on the amounts of lead and antimony found on handsamples by photoluminescence is examined in Section C. In Section D, the effect of the time delay between sampling and firing on the Pb and Sb levels found on the hands of gunshot suicide victims is examined. In Section E, the percentage of gunshot suicide cases that exceed specified threshold values simultaneously for lead and antimony are examined for various weapon categories. The possible methods for overcoming blood effects on photoluminescence analyses are discussed in Section F, and the presence of organic smokeless powder flakes on the hands of gunshot suicide victims is examined in Section G.

A. Handsample Analysis Data from Control Subjects

The amounts of lead and antimony found on handsamples from the backs of the hands of two different types of control subjects are presented in the following two subsections. Subsection 1 contains analysis results for handsamples collected from persons who have died by causes other than gunshot wounds. The results of analyses of handsamples collected in the Los Angeles area from live subjects who are members of certain occupational groups are presented in Subsection 2.

1. Handblanks from coroner control cases. During the field test, a total of 65 handblank samples were collected by the participating laboratories from the backs of the hands of 41 subjects who had died from non-gunshot related causes (see Appendix E). Samples from all but three control subjects were analyzed at The Aerospace Corporation. None of the handblank samples from these 38 subjects was observed to have antimony levels equal to or above 0.01 μg. The remaining handblank samples from the three cases LC-6 through LC-8 were analyzed at one of the participating laboratories and were reported to have antimony levels above 0.01 μg. These values (as well as the antimony values obtained for the suicide cases L-1 through L-15, (discussed in a following section) can be considered upper limit values only since instrumental problems with the spectrofluorometer recorder during these analyses prevented the accurate measurement of excitation spectra baseline values. When the back of the hand with the largest amount of lead from each subject is considered, the average amount of lead found on the handblanks from the 41 control subjects is 0.26 ± 0.36 μg.[a] The subject with the largest amount of lead, 1.68 μg, was reported to have paint present on his hands. If this person is not considered, the average amount of lead found on these control subjects is 0.23 ± 0.28 μg. The percentage distribution of the number of coroner control cases analyzed (excluding the subject with paint on his hands) versus the largest amount of lead from each case is shown in Figure 6. Ninety-five percent of the handblanks have

[a] The standard deviations associated with the average amounts of lead and antimony reported throughout this document are expressed, for simplicity, by the conventional relationship used for data with normal (Gaussian) distributions:

$$\sigma = \sqrt{\sum_i [(x_i - \bar{x})^2]/(n - 1)}$$

However, results obtained during the Gulf General Atomic Study[8] and during gunshot residue characterization studies by SEM particle analyses[4] at The Aerospace Corporation suggest that the amount of gunshot residue found on the hands of people who have fired a gun may more closely obey a log normal than a normal distribution. If log normal statistics are obeyed, it would be more correct to use a logarithmic standard deviation than the conventional standard deviation used here. The observation that the standard deviations calculated in the conventional manner here are often larger than their corresponding means may indicate that log normal statistics are being obeyed. Refer to Pages 28-31 of Reference 4 for a discussion of log normal statistics.

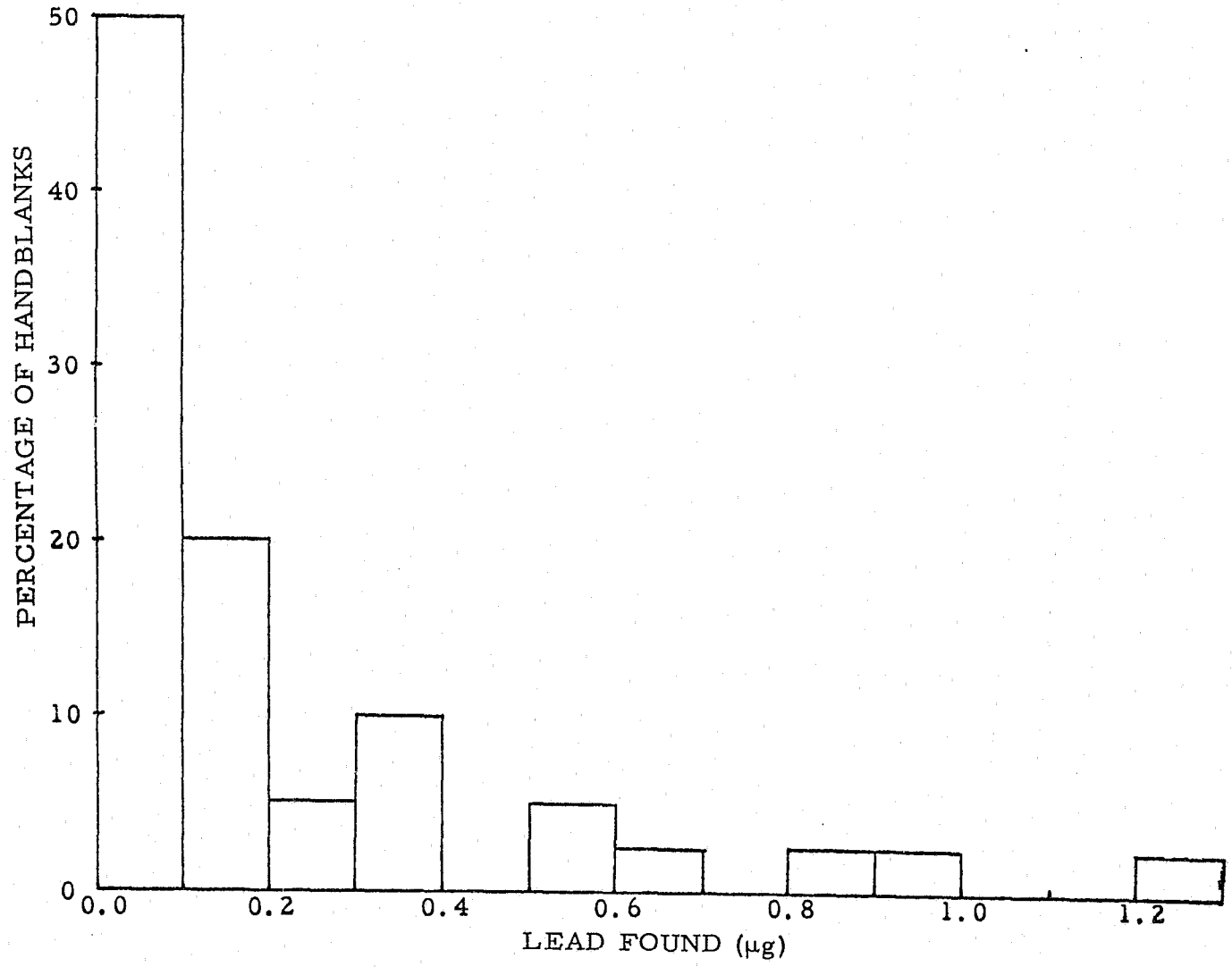


Figure 6. Percentage Distribution of the Number of Coroner Control Cases Analyzed versus the Largest Amount of Lead from Each Case

quantities of lead equal to or less than 0.85 μg, and 90 percent have quantities of lead equal to or less than 0.60 μg. None of the handblanks from the 41 coroner control subjects had levels of lead greater than 0.85 μg and antimony levels equal to or greater than 0.01 μg simultaneously.

2. Occupational handblanks. During the initial phase of the field test, The Aerospace Corporation collected and analyzed handsamples from the backs of the hands of live subjects who were members of various occupations in the Los Angeles area. These data, presented in Appendix F, extend the information obtained in previous studies on the amounts of lead and antimony found on handsamples collected by the adhesive lift technique from persons with expected high occupational exposure to these elements. The data in Appendix F represent the results of analyses of handsamples collected from 31 subjects immediately after each person engaged in his or her work for 15 minutes or longer. The control subjects were not allowed to wash their hands prior to sampling.

Based on the handsample with the largest amount of lead from each subject, the average amount of lead on the backs of the hands of these 31 control subjects was 0.85 ± 0.99 μg. Handsamples from 81 percent of the subjects in Appendix F had lead levels equal to or less than 0.85 μg. Antimony levels below 0.01 μg were obtained for 84 percent of these control subjects. In the previous study,[3] 90 percent of the 45 subjects selected to have high occupational exposure to lead or antimony gave lead levels less than 0.85 μg, while all but one subject gave antimony levels less than 0.01 μg. Handsamples from slightly over 90 percent of the 31 subjects in Appendix F simultaneously had lead levels and antimony levels less then 0.85 μg and 0.01 μg, respectively.

The subjects in Appendix F that yielded lead levels greater than 0.85 μg on at least one handsample included a painter, a lead foil manufacturer, a gas station attendant, a printer, and an assembler/solderer. Antimony levels equal to or greater than 0.01 μg were obtained for a different painter, a carpenter, the same gas station attendant, the same printer, and the same assembler/solderer. Forty-eight percent of the subjects included in Appendix F were smokers. No correlation could be observed from the data to suggest that smoking increases the levels of lead or antimony on the hand.

In the occupational handblank data reported here, considerably less antimony is detected using photoluminescence in conjunction with the adhesive tape lift sampling technique than was found earlier for a similar class of subjects using neutron activation analysis and the paraffin lift sampling technique.[8] Similar results were observed in the previous photoluminescence study.[3] Levels of elements characteristic of gunshot residue collected by various sampling techniques can be expected to differ quantitatively because non-identical areas of the hand are sampled and the efficiency of retrieval of various components of the residue may vary with the sampling method. The lower amounts of antimony found on handblanks using photoluminescence and the adhesive lift technique should lead to the use of antimony photoluminescence thresholds substantially lower than the 0.2 μg level suggested by ATF for gunshot residue detection by neutron activation analysis and atomic adsorption spectroscopy.

3. Comparison of the amount of lead found on both hands of coroner and occupational control subjects. Some criminalistics laboratories that use bulk elemental analyses to determine whether a person may have recently fired a gun consider not only the absolute amounts of the elements which are characteristic of gunshot residue on the hand, but also the ratio of the amounts of these elements found on one hand to that on the other. Although data are not generally available which compare background levels of these elements on both hands of people who have not recently fired a gun,[a] it has been presumed that similar amounts of these elements would be found on each hand of a given subject due to environmental or occupational exposure.

Examination of the handblank data in Appendices E and F reveals that this assumption may often be valid since similar amounts of lead are usually found on handsamples from the backs of each hand of any given coroner control subject or occupational control subject. Of the 16 coroner control subjects yielding at least 0.05 μg of lead on both handsamples, 8 of the subjects had ratios of 1.5 or less for the amount of lead found on the handsample with the most lead to the amount found on the handsample with the least lead. Only two of these subjects had ratios greater than 2.0, while the largest ratio obtained for the coroner

[a]The National Bureau of Standards recently carried out a comparison of the amounts of elements characteristic of gunshot residue on handsamples from both hands of control subjects who have not recently fired a gun. The results of this study have not yet been published.

control subjects was 3.0. Of the 23 occupational control subjects with at least 0.05 μg of lead on both handsamples, 16 had ratios of 1.5 or less for the amount of lead found on the handsample with the most lead to that with the least lead. A ratio greater than 2.0 was obtained for only one occupational control subject. This subject had a ratio of 2.9. However, it may be significant that even in this limited group some subjects exhibited ratios which differed from unity. In a typical occupational environment, one hand may hold a tool and the other may hold an object upon which work is being performed. Whether one or the other hand receives a larger amount of contamination, or whether both receive approximately equal amounts would depend on the nature of the operation. Similar arguments can be made with reference to firing a gun, since the firing can be done one-handed or two-handed. Especially in suicides, one hand often holds the barrel and the other hand is used to pull the trigger. Attaching too much significance to the foregoing ratios may result in invalid conclusions.

B. Comparison of Field Test Data with Previous Test Firing Data

Where the information is available, the results in Appendix E are categorized in Table 2 according to weapon type, caliber, and bullet type; and whether blood was reported to be present on the hand sampled, on the disk after sampling, or in the HCl solution following its removal from the sampling disk. To calculate the averages in Table 2, values from Appendix E were chosen in each case for the back of the hand that had the largest amount of lead and antimony.

The Aerospace Corporation's previous photoluminescence work[3] showed that larger average amounts of lead and antimony are deposited on the hand during .38 caliber revolver test firings than during .22 caliber revolver test firings. A similar trend is seen in the limited data of Table 2 for gunshot suicide cases both when blood is present and when blood is not present on the hand. Comparison of the data in Table 2 with results from the previous study[3] reveals that generally lower lead and antimony levels are found on handsamples from gunshot suicide cases involving .38 and .22 revolvers than are found on the corresponding handsamples collected immediately after one round test firings of .38 and .22 revolvers.

The average amounts of lead and antimony found on handsamples collected in suicide cases involving .22 revolvers, rifles, and shotguns are observed in Table 2 to be close to the average amounts of these elements found on handsamples collected from coroner control subjects who died of causes other than gunshot wounds.

C. Effect of Blood on Pb and Sb Detectability by Photoluminescence

The average amount of lead and antimony found in Table 2 for .38 revolver firings in which bare lead bullets were used is lower when blood was present on the hand sampled than when blood was absent. However, the numbers of cases in each category are too small to allow a statistically firm conclusion to be drawn that the amounts of lead and antimony found on handsamples by photoluminescence is decreased by the presence of blood on the hand. The data are suggestive, however, of such an effect.

For this reason, controlled laboratory experiments were conducted at The Aerospace Corporation to examine the effect of blood on lead and antimony analyses by photoluminescence. The data in Table 3 represent the analysis results of samples taken from the back of the firing hand immediately after one-round test firings of a .380 Browning automatic pistol with Remington fully-jacketed ammunition. Handsamples 1 through 4 in Table 4 were analyzed directly. Various quantities of blood were added to the eight remaining sampling disks after collection. For samples 5 through 8 in Table 3, various quantities of a 10% solution by volume (for ease of quantitative application) of whole blood in distilled water were applied to the sampling disks, spread uniformly across the disks, and allowed to dry. A similar procedure was used for handsamples 9 through 12, except that various amounts of whole blood were applied directly. Comparison of the amounts of lead and antimony found on handsamples to which blood had been added with the average amounts of these elements on samples without added blood indicates that decreasing amounts of lead and antimony are generally found by photoluminescence as a function of increasing amounts of blood on the sampling disks.

Table 2. Blood Effects on the Average Amounts of Lead and Antimony on the Handsamples from Gunshot Suicide Victims

Gun Type	No Blood Present			Blood Present		
	Avg Pb µg	Avg Sb* µg	Number of Samples (n); Bullet Type†	Avg Pb µg	Avg Sb* µg	Number of Samples (n); Bullet Type†
Revolvers						
.45	0.15	ND	(1) FJ	---	---	---
.44	---	---	---	4.25	0.10	(1) ?
.38	2.68 [0.6 - 4.45]‡ 2.92 [0.85 - 5.00]	0.24 [ND - 0.5][a] 0.10 [ND - 0.2]	(6) L (2) ?	1.02 [ND - 2.4] 0.44 [0.2 - 0.65]	0.02 [ND - 0.10] <0.01[b]	(7) L (3) 1SJ, 1FJ
.357	3.2	ND	(1) SJ	0.18	---[c]	(1) L
.32	2.2	0.17	(1) ?	---	---	---
.22	1.03 [0.2 - 5.4] 0.77 [0.28 - 1.6]	<0.01[d] <0.01[f]	(8) 7L, 1P (5) 4SJ, 1?	0.56 [0.4 - 0.74]	ND[e]	(5) 3L, 1P, 1 ?
Pistols						
.45	---	---	---	1.79	---[g]	(1) L
9 mm	---	---	---	---	---	---
.380	2.40	0.28	(1) FJ	---	---	---
.32	0.20	0.02	(1) ?	---	---	---
.25	0.46 [0.07 - 0.9]	ND	(3) 1SJ, 2FJ	0.77	---[h]	(1) ?
.22	---	---	---	---	---	---
Rifles						
.308	---	---	---	0.4	ND	(1) ?
.30	---	---	---	0.05	<0.01	(1) L
.22	0.44 [ND - 0.7] 0.52	ND[i] ---	(3) P (1) SJ	0.42	ND	(1) ?
Shotguns						
12 G	0.65	ND	(1)	0.41 [ND - 0.88]	0.03 [ND - 0.07]	(3)
16 G	0.14	<0.01	(1)	0.55 [0.13 - 0.97]	ND[j]	(2)
.410	0.8	ND	(1)	0.24	---[k]	(1)

*antimony averages exclude the following cases:

a. L-4
b. L-5
c. L-14
d. L-3, L-7
e. L-1, L-2, L-15
f. L-11, L-12
g. L-13
h. L-6
i. L-10
j. L-9
k. L-8

‡ values in brackets represent ranges for lead and antimony

† type of bullet used: L = bare lead, SJ = semi-jacketed, FJ = fully jacketed, P = Plated, ? = Unknown

ND = Not Detectable

Table 3. Effect of Blood on Lead and Antimony Levels from .380 Autopistol Firings[a]

Sample No.	Amount of Blood Present on Disk	Lead Found µg	Antimony Found µg	Ratio of Pb Found to Ave. Pb from Samples 1-4	Ratio of Sb Found to Ave. Sb from Samples 1-4
1	0	0.65	0.09		
2	0	0.85	0.19		
3	0	1.80	1.16		
4	0	0.73	0.11		
	Average of Samples 1 thru 4:	1.01 ± 0.54	0.39 ± 0.52		
5	0.001 ml[b]	0.48	0.09	0.48	0.23
6	0.004 ml[b]	0.50	0.32	0.50	0.82
7	0.008 ml[b]	0.15	0.07	0.15	0.18
8	0.015 ml[b]	0.18	0.08	0.18	0.21
9	1 drop[c]	0.08	ND	0.08	ND
10	2 drops[c]	0.15	0.01	0.15	0.03
11	3 drops[c]	0.05	0.02	0.05	0.05
12	4 drops[c]	0.08	0.02	0.08	0.05

[a]Remington 95-grain, round-nose, fully jacketed cartridges.

[b]Whole blood was diluted into solution, then pipetted onto the sampling disk. These values represent the amount of blood present on the disk prior to allowing the solution to dry.

[c]Whole blood added directly to the disk.

ND = not detectable

Table 4. Percentage of Gunshot Suicide Cases Simultaneously Having Greater Than 0.85 μg of Lead and Equal to or Greater Than 0.01 μg of Antimony[a]

	.38 Revolvers	.22 Revolvers	Revolvers Other Than .38 and .22	Autopistols of Various Calibers	Rifles of Various Calibers	Shotguns	All Guns	Handblanks from Subjects who Died of Non-Gunshot-Related Causes	Handblanks from Live Subjects with Expected Occupational Exposure to Pb and Sb
Average Pb μg	1.69 ± 1.59	0.82 ± 1.15	2.00 ± 1.82	0.94 ± 0.86	0.37 ± 0.26	0.46 ± 0.37	1.06 ± 1.28	0.26 ± 0.36	0.85 ± 0.99
Average Sb[b] μg	43.8% ND[c] 0.18 ± 0.16	83.3% ND[c] <0.01	50.0% ND[c] 0.14 ± 0.05	40.0% ND[c] 0.10 ± 0.15	71.4% ND[c] <0.01	57.1% ND[c] 0.03 ± 0.04	58.8% ND[c] 0.11 ± 0.14	89.5% ND[c] <0.01	67.7% ND[c] 0.04 ± 0.06
Percentage of cases having >0.85 μg Pb	55.6% (18)[d]	10.5% (19)[d]	60% (5)[d]	42.9% (7)[d]	0% (8)[d]	22.2% (9)[d]	30.3% (66)[d]	5.0% (40)[d]	19.4% (31)[d]
Percentage of cases having ≥0.01 μg Sb[b]	50% (16)[d]	0% (12)[d]	50% (4)[d]	60% (5)[d]	0% (7)[d]	14.3% (7)[d]	27.5% (51)[d]	0% (38)[d]	16.1% (31)[d]
Percentage of cases having >0.85 μg Pb and ≥0.01 μg Sb[b]	50% (16)[d]	0% (12)[d]	50% (4)[d]	40% (5)[d]	0% (7)[d]	14.3% (7)[d]	25.5% (51)[d]	0% (40)[d]	9.7% (31)[d]

[a] The foregoing data (where blood effects are ignored) represent lower limits to the results that would be obtained in the absence of blood effects.

[b] The average value given for antimony was calculated using only values for which antimony was detectable.

[c] Not detectable.

[d] Number in parentheses represents number of cases.

From Table 3, it is apparent that small amounts of blood on handsamples can decrease the amounts of lead and antimony found by photoluminescence. Small amounts of blood may not always be readily detected visually on handsamples after collection. However, some indication as to the presence of blood on a sampling disk may be obtained by examination of the excitation spectrum recorded to determine the presence of antimony. Figures 7(a) and 7(b) compare the excitation spectra that were recorded to determine the levels of antimony on Samples 2 and 5 in Table 3. Figure 7 (c) shows the excitation spectrum obtained for approximately the same quantity of blood as was present on Sample 5 shown in Figure 7(b), but with antimony absent. In addition to the decrease in the excitation spectral intensity observed for the chloride ion complex(es) of antimony, a distorted baseline for the excitation spectrum is noted in Figure 7(b) due to the presence of blood.

D. Possible Effect of Time Delay Between Sampling and Firing on Pb and Sb Levels on Hands of Suicide Victims

The results shown in Appendix E were examined to determine whether the length of time between a suicide and when a victim's hands are sampled can affect the amount of gunshot residue found. The analysis data in Appendix E, for blood-free handsamples from cases involving any handgun/cartridge combination giving lead or antimony levels well above background levels, suggests a decreasing overall trend in the amount of lead found with an increase in the time between firing and sampling. Nearly all of the handgun cases reported in Appendix E that had greater than 2.0 μg of lead on at least one handsample can be observed to have been collected within 5 hours of firing. Most of the handgun cases collected within 5 hours of firing that gave less than 1.0 μg of lead involved the use of jacketed bullets and/or the handsamples from these cases were observed to have blood present on them after collection. The smaller amounts of lead found on the latter samples thus might be expected. The limited analysis results for most of the remaining handgun cases in Appendix E suggest that the amount of lead found generally decreases with an increase in the time between firing and sampling.

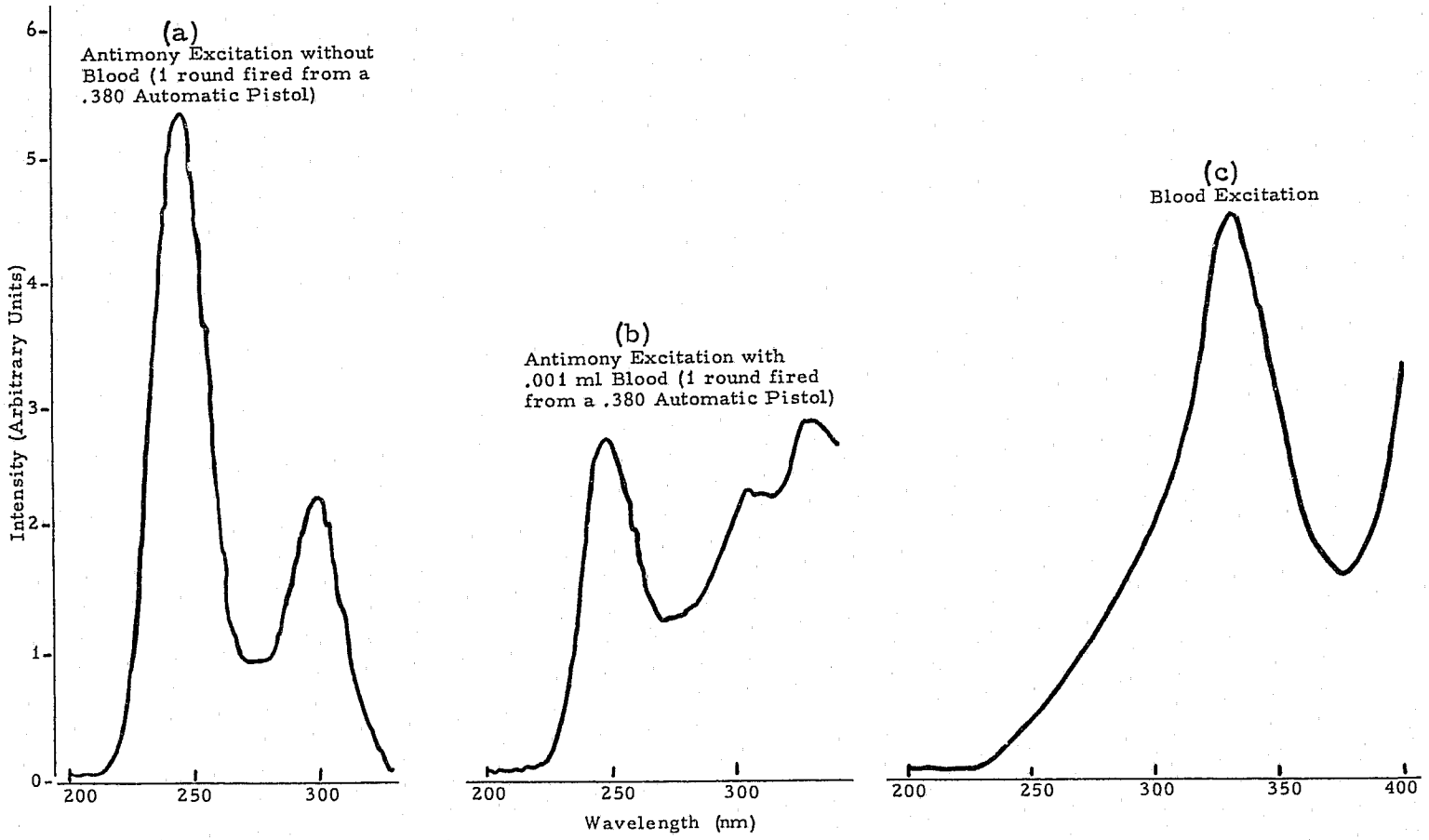


Figure 7 Blood Effects on Sb Excitation Spectra (660 nm Emission)

If this apparent loss of gunshot residue with time from the hands of suicide victims is real, it is still substantially slower than the order of magnitude loss observed from the hands of normally active live subjects in the first hour after firing. It is not known why this slow loss might occur from the hands of immobile subjects such as suicide victims. The decreasing amounts of lead observed with time may reflect increased losses due to the greater opportunity for the victims' hands to be disturbed with time. Another possibility is that with increasing time, increasing amounts of decomposition products from the skin may form which either quench the luminescence of the lead (II) and antimony (III) chloride complexes and/or react with lead (II) or antimony (III) ions in some manner to inhibit their quantitative recovery from the hand. That a decrease in the amounts of lead and antimony found on the hands of a gunshot suicide victim does not always occur with time, however, is indicated by the large amounts of lead and antimony (4.45 μg, and, 0.50 μg, respectively) found on the back of one of the hands of a subject sampled > 10 days after firing (see Case No. P-15, Appendix E). Much more data from suicide cases involving particular handgun/cartridge combinations giving copious lead and/or antimony levels are needed before a firing-sampling time delay effect on the amounts of these elements detected on victims' hands can be confirmed, and before a mechanism for this apparent loss can be established.

E. Handsample Analysis Data from Gunshot Suicide Victims

The averages of the largest lead and antimony values from each gunshot suicide case are listed in Table 4 according to various weapon categories. These averages were calculated without distinguishing between cases in which blood was observed on handsamples after collection and cases in which blood was absent.

Also listed in Table 4 for each weapon category are the percentage of cases reported with: (1) lead levels above 0.85 μg, (2) antimony levels equal to or above 0.01 μg, and (3) lead levels above 0.85 μg and antimony levels equal to or greater than 0.01 μg simultaneously.

Approximately 50 percent of the gunshot suicide cases were observed to have blood present on at least one handsample after collection. The average lead and antimony values and the percentage of cases exceeding various thresholds in each weapon category in Table 4 might be expected to increase significantly if the deleterious effects of blood on the photoluminescence analyses could be overcome. For this reason, the results in Table 4 (where blood effects are ignored) represent lower limits to the results that would be obtained in the absence of blood effects.

1. Percentage of cases with lead levels above 0.85 μg. The data in Table 4 indicate that lead values greater than 0.85 μg were found on handsamples from the back of at least one hand of each victim in 53 percent of the cases (16 of 30) involving all handguns other than .22 revolvers. Levels of lead greater than 0.85 μg were observed for 12 percent of the cases (2 of 17) involving long guns, and only 11 percent of the cases (2 of 19) involving .22 revolvers. When cases involving all guns are considered, 30 percent (20 of 66) exceeded 0.85 μg of lead. By comparison, 95 percent of the coroner control subjects were observed in Section A.1 of this chapter to have lead values equal to or below 0.85 μg.

2. Percentage of cases with antimony levels equal to or greater than 0.01 μg. Excluding from consideration the upper limit antimony values obtained in cases L-1 through L-15, antimony levels equal to or greater than 0.01 μg were found on handsamples from the back of at least one hand of each suicide victim in approximately fifty percent of the cases involving handguns other than .22 revolvers. None of ten .22 revolver cases, and only one of 14 cases involving long guns gave antimony levels equal to or greater than 0.01 μg. Antimony values equal to or greater than 0.01 μg were obtained in 29 percent of the cases (14 of 29) involving all guns. None of the coroner control cases had antimony values equal to or greater than 0.01 μg upon exclusion of the upper limit values obtained in cases LC-6 through LC 8.

3. Percentage of cases with lead levels greater than 0.85 μg and antimony levels equal to or greater than 0.01 μg simultaneously. The occupational and coroner control handblank data obtained during the field

test are too limited to allow selection of the optimum threshold values for distinguishing firing handsamples from nonfiring handsamples by the photoluminescence technique. It was noted previously, however, that handsamples from slightly greater than 90 percent of the control subjects that were expected to have high levels of lead and antimony on their hands due to occupational exposure had levels for these elements simultaneously below 0.85 μg and 0.01 μg, respectively. It would be expected that much closer to 100 percent of subjects chosen at random from the general population would have handsample levels of lead and antimony simultaneously below 0.85 μg and 0.01 μg, respectively. This is indicated by the observation that the lead and antimony levels on handsamples from 100 percent of the coroner control cases were simultaneously below these limits.

The data in Table 4 show that if lead levels greater than 0.85 μg in conjunction with antimony levels equal to or greater than 0.01 μg are taken as being suggestive of the presence of gunshot residue on handsamples; correct identification of gunshot residue is obtained for 48 percent of the cases (12 of 25) involving all handguns other than .22 revolvers for which lead and antimony analyses are available. Using the same criteria, correct identification of gunshot residue was obtained for only one of seven of the cases involving shotguns, and for none of the cases involving either .22 revolvers or rifles of various caliber.

The low success rate obtained by the photoluminescence technique for cases involving rifles and shotguns in Table 4 is expected on the basis of the sparse amounts of gunshot residue found by SEM particle analysis[4] on handsamples from persons who have recently fired these guns. Near background levels only of elements characteristic of gunshot residue have been found by other bulk elemental techniques on handsamples collected from subjects who have test fired rifles and shotguns. On the basis of our previously published photoluminescence analysis results of handsamples taken during .22 revolver test firings,[3] a higher success rate might be expected than is observed in Table 4 for cases involving .22 revolvers. The reason

for this discrepancy is not known. The low success rate for cases involving .22 revolvers in this study, however, is consistent with the fact that the Bureau of Alcohol, Tobacco, and Firearms will not accept .22 revolver cases for barium and antimony analyses due to a similar low success rate for these cases by atomic absorption spectroscopy.

The lower limit 48 percent success rate (12 of 25 cases) obtained in Table 4 for all handguns other than .22 revolvers should increase significantly if the adverse effects of blood on the photoluminescence analyses can be eliminated. For example, 8 of the 16 cases involving .38 revolvers gave lead and antimony values that were simultaneously below their respective 0.85 μg and 0.01 μg threshold levels. Of these eight .38 revolver cases, six had blood present on at least one handsample after collection. Of the eight .38 revolver cases exceeding the limits simultaneously, only 2 had a significant amount of blood, and one had a slight amount of blood. For the .38 revolver cases without blood, the suggested thresholds were exceeded by 5 out of 7 cases (71%), and for those with blood, 3 out of 9 cases (33%) exceeded the limit.

The lower limit results in Table 5 for handguns other than .22 revolvers thus suggest that the photoluminescence technique should be useful in gunshot suicide investigations if the adverse effects of blood on the photoluminescence analyses can be overcome. The previous Aerospace Corporation photoluminescence study[3] showed that under optimum conditions (samples collected from the firing hands of live subjects immediately following one-round indoor test firings) lead and antimony levels above the foregoing simultaneous threshold levels were obtained for 95 percent (41 of 43) of firings of handguns other than .22 revolvers and for 88 percent (15 of 17) of .22 revolver firings.

---

[a]Of the nine cases involving handguns other than .38 or .22 revolvers, five gave lead and antimony levels below these simultaneous threshold levels. None of the handsamples from these five cases had blood on them. The below-threshold levels in these cases may be the result of the type of bullet used. Four of these cases involved jacketed bullets, while the fifth was of an unknown bullet type.

F. Blood Effects on Atomic Absorption Analyses, Possible Methods to Overcome Blood Effects on Photoluminescence Analyses

In the analysis of handsamples for barium and antimony by atomic absorption spectroscopy, severe problems are also encountered in the contamination of the sample collection surface (usually a cotton swab) with blood. Contamination by blood may make the swab impervious to the penetration of the dilute nitric acid used to leach gunshot residue from the swab for analysis. By this effect the measured levels of barium and antimony will thus be lower than those actually present on the sample. The presence of blood on handsamples must also be removed prior to sample atomization by plasma ashing or some other technique to avoid high background absorption due to light scattering by particulate matter from the blood.

Due to the problems encountered with blood effects on the detection of gunshot residue by both atomic absorption spectroscopy and the photoluminescence technique, it is expected that both methods would be roughly equivalent in their usefulness to detect gunshot residue on the hands of gunshot suicide victims.

A recent paper[12] describes a low pressure oxygen plasma technique that can be used prior to atomic absorption spectroscopy for the pre-ashing of gunshot residue samples that are contaminated with blood, dirt, or grease. Because this plasma ashing technique can be used on other types of collection materials including tape, it might be a useful technique for eliminating blood from handsamples prior to photoluminescence analysis. Since the plasma ashing technique is an oxidative procedure, it may be necessary to follow the ashing step by application of a chemical reducing agent to assure that lead and antimony ions are in their +2 and +3 oxidation states, respectively, prior to photoluminescence analysis.

An oxidative procedure alternative to plasma ashing that may be useful in eliminating the adverse effects of blood on the photoluminescence analyses for lead and antimony was suggested by personnel at the Los Angeles County Medical Examiner's Office. This technique involves the application to the

sampling disk of a chemical oxidizing agent such as hydrogen peroxide. This step would then have to be followed by the application of a suitable chemical reducing agent to retrieve the proper oxidation states of lead and antimony for photoluminescence analysis. Although preliminary experiments conducted at both the Los Angeles County Medical Examiner's Office and The Aerospace Corporation suggest that such a procedure may be feasible,[13] the limited time available for the field test has prevented an acceptable process from being developed.

G. Presence of Organic Smokeless Powder Flakes on the Hands of Gunshot Suicide Victims

During the field test, each of the participating laboratories examined the hands of gunshot suicide victims for the presence of organic gunpowder flakes and tabulated the frequency and quantity of their occurrence for statistical purposes. These laboratories reported that the presence of at least one organic flake could be observed on the hands of 10 to 15 percent of the gunshot suicide victims. Generally, only one or two flakes were observed on the hands of these suicide victims. The frequency and quantity of occurrence of organic flakes observed during the field test was slightly less than that observed at The Aerospace Corporation during the investigation of apparent gunshot suicide cases by the SEM particle analysis technique. In the SEM work, at least one organic flake was observed on the hands of 22 percent (10 of 45) of the apparent gunshot suicide victims.

In experiments conducted at The Aerospace Corporation, only about one-third of the organic flakes observed visually in test firings could be proven to be of nitrocellulose or nitroglycerine origin by currently used thin layer chromatographic procedures.

CHAPTER V. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

A. Conclusions

From the present limited data, a conservative criterion for presuming that gunshot residue is present on a handsample collected by the adhesive lift technique from the back of a subject's hand appears to be that the lead and antimony levels (as measured by the photoluminescence technique) simultaneously exceed the values 0.85 μg and 0.01 μg, respectively. This tentative conclusion is based on the observation that 100 percent of the coroner control subjects and slightly greater than 90 percent of the occupational control subjects had lead and antimony levels below these levels simultaneously.

The amounts of these elements on the hands of coroner control subjects are expected to be similar to those found on the hands of members selected at random from the general population. The amounts of these elements on occupational control subjects should be substantially greater than those from the general population.

The presence of blood on handsamples has an unfavorable effect on the detectability of lead and antimony by the photoluminescence technique. The effect of blood on these analyses currently constitutes a major problem that must be overcome before the photoluminescence technique can achieve its full potential and be established as a field method for the investigation of gunshot suicide cases. It is expected that either the low pressure oxygen plasma ashing technique, which is currently used to overcome the adverse effects of blood on atomic absorption analyses, or some chemical oxidation technique should be useful in eliminating blood effects on photoluminescence analyses. The adoption of these techniques will likely be dependent on the possibility of using a reducing agent to restore the lead and antimony ions to their respective +2 and +3 oxidation states following either of the foregoing oxidative processes. The concentration and/or the reducing potential of the reagent used for this purpose appear to be critical variables that need to be determined.

Unless the identification procedures used for these flakes become more efficient, it is expected that conclusive identification of organic gunpowder flakes by this technique would be possible at the most for about 7 percent of all gunshot suicide cases. This low success rate in the identification of the presence of organic flakes would not justify the time and effort required for their identification.

B. Recommendation

Besides attempts to eliminate blood effects on photoluminescence analyses, more extensive data need to be collected from suicide cases involving particular handgun/cartridge combinations giving copious lead and/or antimony levels. These data are needed to establish whether the amounts of lead and antimony detected by photoluminescence on the hands of suicide victims decline with increasing time delays between firing and sampling.

APPENDIX A. FACT SHEET FOR GUNSHOT SUICIDE CASES

Please record the following information for each gunshot suicide victim:

Case number_____

Victim's Name or ID_____ Sex_____

Victim's Occupation_____ Activity Prior to Shooting_____

Hours between Firing and Sampling _____ Indoors_____ Outdoors_____ No. shots____

Weapon Type_____ Caliber_____ Make/Model_____ Barrel Length_____

Ammo Brand/Type (High Vel. Standard) _____

Bullet Type_____ Bullet Weight_____ Jacketed_____ Semi-Jack._____ Plated_____ Bare Lead_____

Sample Identifications (labels)

Right Web, Back _____, Right Wrist _____

Left Web, Back _____, Left Wrist _____

Special Comments:

APPENDIX B. GUNSHOT RESIDUE DETECTION BY PHOTOLUMINESCENCE

A. Instructions for Sampling Gunshot Suicide Victims

The basic sampling device is a disk of aluminum, one inch in diameter and about 3/8-inch high. It is cut from one-inch bar stock, using alloys 6063 (preferably) or 1100. These are the only aluminum alloys that are readily available in bar stock and at the same time are low enough in those heavier elements that are of interest in gunshot residue analysis. A one-inch square of scotch transfer tape No. 465 is placed on the disk, adhesive side down. When the disk is to be used, the paper is pulled off, leaving the adhesive on the disk.

To sample a person's hand, the disk is pressed repeatedly against the hand, adhesive side down, and is moved from place to place until the disk has lost its stickiness. The disk should be firmly pressed straight down and lifted straight up; it should not be slid or rotated on the skin (see Figure 8).

Figure 8. Use of the Sampling Disk

The pattern of movement should start in the web area in and just behind the junction of the thumb and forefinger. The movement should then be along the backs of the thumb and forefinger, the back of the forefinger, the back of the hand further behind the web, the backs of the middle and fourth finger, and finally the far back of the hand. In suicides, it may often be productive to also sample the inside of the wrists because of the sharp angle at which the gun may have been held. The sampling of additional areas should be continued as long as the disk sticks to the skin, but it should be stopped when disk stickiness is lost.

The sampling should be performed as soon after the shooting as possible. The victim's hand should not be washed or rubbed prior to sampling, and the victim should not be fingerprinted prior to sampling. No hand swabs for other types of analysis should be taken prior to sampling.

Every effort should be made to obtain full information on the type of gun and ammunition used. This information should be entered on the data sheet.

When the gunshot residue has been collected on the sampling disks, the disks should be protected from dust and environmental contaminants. If this precuation is taken, the disks which contain the gunshot residue may be stored indefinitely prior to dissolution of the gunshot residue from the disks with hydrochloric acid for photoluminescence analysis.

APPENDIX C. ANALYSIS PROCEDURES FOR GUNSHOT RESIDUE FROM SUICIDE VICTIMS BY THE PHOTOLUMINESCENCE TECHNIQUE

The photoluminescence technique for detecting gunshot residue is a relatively simple procedure. However, because of the rapid decline of the presence of gunshot residue on the hands of an active living suspect after he has fired a gun, this technique is not as successful as SEM particle analysis. In suicide cases, however, since the victim generally remains immobile, the luminescence method may be adequate and is less expensive and less time-consuming than particle analysis.

This outline provides instructions for the luminescence analysis of gunshot residue and gives a description of the equipment necessary for this analysis.

Summary of Equipment:

Each Medical Examiner should have all of the equipment necessary for analysis of gunshot residue using the photoluminescence technique. The required equipment includes:

1. Spectrofluorometer equipped with a Xenon lamp excitation source, and both an excitation and an emission monochromator.
2. Liquid Nitrogen availability.
3. Sampling Disks each of which consists of a one-inch diameter aluminum disk covered on one surface with Scotch transfer tape #465.
4. Quartz Dewar Flask with outer collar and inner sample tube fitting.
5. Sample Tubes with Suprasil tips.
6. F G-10 Emission Filter.
7. Hamamatsu R-777 Photomultiplier Tube which is red sensitive to maximize detection of antimony.
8. Stock Compounds - lead nitrate [$Pb(NO_3)_2$, F.W. = 331.23] and antimony potassium tartrate [$SbKC_4H_4O_7 \cdot 1/2\ H_2O$, F.W. = 333.93].

Procedure:

Prior to the analysis of the gunshot residue samples, the preparation of Pb and Sb calibration curves is necessary. These calibration curves will be used to quantitatively determine the amount of Pb and Sb present in the samples. The Handsample Data section of the publication entitled "Gunshot Residue Detection Using Inorganic Luminescence" can be used as a guide for determining typical quantities of residue often found on the hands after a firing.

I. Preparation of Stock Solutions:

A. Dissolve .160 grams $Pb(NO_3)_2$ in 500ml. distilled H_2O for a lead concentration of 200μg/ml.

B. Dissolve .166 grams antimony potassium tartrate in 1000ml. distilled H_2O for an antimony concentration of 60μg/ml.

C. Stock Solutions can be stored indefinitely.

II. Preparation of Standards:

A. Use 7M HCl for the dilution of the stock solutions to the desired standard concentrations. Seven M HCl forms a clear glass when frozen at liquid nitrogen temperature (77K). The 7M HCl should be prepared from reagent grade (12M) concentrated hydrochloric acid (for an antimony standard with a concentration of 6.0μg/ml, dilute 10.0 ml of antimony stock solution in 90.0 ml of 7M HCl).

B. Typical concentrations of standard solutions that can be used are: (μg/ml)

Pb	Sb
20.0	6.0
15.0	5.0
12.0	4.0
10.0	3.0
8.0	2.0
6.0	1.0
5.0	0.5
4.0	0.2
3.0	0.15
2.0	0.10
1.0	0.05
0.2	0.02
0.08	0.01
	0.005
	0.002

(It should be noted that the HCl concentration will vary in the standard solutions due to the varying ratios of stock solution to HCl for each concentration of Pb or Sb prepared. This will not effect the results.)

C. Analyze lead standards within the same day the HCl is added.

D. Analyze antimony standards within a few hours following the addition of HCl.

III. Analysis of Lead Standards:

A. Allow a sufficient amount of time (5-10 min.) for lamp to reach maximum signal after instrument is turned on.

B. Adjust excitation and emission band pass settings to approximately 1.0 nm and 14 nm, respectively.

For Aminco-Bowman spectrofluorometers equipped with 600 line/nm excitation and emission monochromators this will require the use of the following instrumental settings:

1. Excitation Monochromator:
   a. entrance slit (between lamp and monochromator) 0.5 mm.
   b. monochromator baffle slit (exit shutter) 2.0 mm.
   c. drop-in cell slit (inside sample compartment on excitation side) 0.1 mm.
2. Emission Monochromator:
   a. drop-in cell slit (inside sample compartment on emission side) 2.0 mm.
   b. monochromator baffle slit (entrance shutter) 2.0 mm

C. Place 0.5 ml. of standard solution into sample tube.

D. Place sample tube into quartz Dewar flask filled with liquid nitrogen. (This is done quickly to insure the formation of clear glass.)

E. Set emission monochromator at 390 nm.

F. Cover the sample compartment of the instrument with a dark cloth to prevent room light from entering the emission monochromator.

G. Record the excitation spectrum; Pb maximum occurs at 276 nm.

H. Rapidly heat the sample tube by placing it, directed away from the body, into a beaker of warm water. (This prevents cracking the tube which may occur due to differences in the coefficients of expansion of the sample tube and the sample.)

I. Clean sample tubes by:
   1. shaking the standard solution out of the tube.
   2. rinsing several times with distilled water.
   3. rinsing once with methanol.
   4. placing sample tubes in an oven to dry.

IV. Analysis of Antimony Standards:

A. Allow a sufficient amount of time for the lamp to warm up.

B. Adjust excitation and emission bandpass settings to approximately 6.6 nm and 26 nm, respectively.

For Aminco-Bowman spectrofluorometers equipped with 600 line/mm excitation and emission monochromators, this will require the use of the following instrumental settings:

1. Excitation Monochromator:

   a. entrance slit (between lamp and monochromator) 2.0 mm.
   b. monochromator baffle slit (exit shutter) 2.0 mm.
   c. drop-in cell slit (inside sample compartment) 4.0 mm.

2. Emission Monochromator:

   a. drop-in cell slit (inside sample compartment) 2.0 mm.
   b. monochromator baffle slit (entrance shutter) 2.0 mm.

C. Place 0.5 ml of standard solution into sample tube.

D. Place sample tube into quartz Dewar flask filled with liquid nitrogen.

E. Set emission monochromator at 660 nm.

F. Place FG-10 emission filter between sample and emission monochromator entrance slit.

G. Cover the sample compartment of the instrument with a dark cloth to prevent room light from entering the monochromator.

H. Record the excitation spectra; Sb maxima occur at 250 nm and 300 nm.

I. Rapidly heat the sample tube.

J. Clean sample tubes (using procedure in III-I).

V. Preparation of Calibration Curves:

A. Plot fluorescence intensity (using arbitrary units) vs concentration (μg/ml.)

B. Plot two curves for antimony using the excitation peak at 250 nm:

1. using all of the values analyzed.
2. using an expanded scale to plot the fluorescence intensity vs concentrations less than 0.2 μg/ml.

VI. Analysis of Gunshot Residue Procedure:

A. The sampling from the hands of the gunshot victim is done according to the instructions that were previously provided.

B. With the disk lying on a flat surface with the adhesive side up, accurately pipet 0.5ml 7M HCl onto the sampling disk.

C. Allow HCl to soak and react for ~ 2 minutes and no more than three minutes.

D. Use a Pasteur pipet to transfer the solution into a Suprasil sample tube.

E. Analyze the gunshot residue sample by the procedure described for analysis of standards.

F. Analyze 2 or 3 standards for both Pb and Sb along with the gunshot residue sample to establish a point of reference on each calibration curve. This prevents error due to changes in the intensity of the lamp source.

Results:

The concentration of lead and antimony in the gunshot residue sample is determined by a comparison with the calibration curves. The concentrations of lead and antimony responsible for the observed peak heights are read from the calibration plot in units of μg/ml. The quantities (in units of μg) of lead and antimony present on the disk are calculated by multiplying the concentrations found for each of these elements (in μg/ml) by the volume of 7M HCl pipetted onto the disk (0.5 ml).

APPENDIX D. A THIN LAYER CHROMATOGRAPHIC PROCEDURE FOR CONFIRMING THE PRESENCE AND IDENTITY OF SMOKELESS POWDER FLAKES

This appendix contains instructions for a rapid and easily performed analysis which can identify unburnt or partially burnt smokeless powder flakes found on the hands or clothing of a suspect or suicide victim.

This analysis is based on:

a. particle morphology and solubility in acetone,

b. R_f values when chromatographed on TLC plates, and

c. specificity of visualizing reagent.

Summary

Unburnt smokeless powder flakes from single base powders consist of nitrocellulose and stabilizers. Double base powders also contain up to 40 percent nitroglycerine by weight.

The Saltzman-Greiss reagent*, which is used in this procedure, tests for nitrite ion that is released from nitroglycerine (NG) and nitrocellulose (NC) by alkaline hydrolysis. The specificity of this analysis is increased by sequential chromatography on thin layer silica gel plates, using solvent systems which will separate NC from NG and will also distinguish propellant grade nitrocellulose from non-propellant grade due to differences in the cellulose polymer chain length. Non-propellant nitrocellulose is used as a base for some lacquers, inks, resins and films.

Materials Required:

1. Saltzman-Greiss reagent: [14]
   a. Prepare: Stock solution of .1% by weight N-(1-napthyl) ethylene diamine dihydrochloride in distilled H_2O.
   b. Dilute 14 ml glacial acetic acid with 80 ml distilled water and
   c. Dissolve 0.5 g sulfanilic acid in it.
   d. Add 2 ml of the .1% stock solution from (a) above.
   e. Add distilled H_2O to a final volume of 100 ml.
   f. Store in a brown bottle away from light. The prepared reagent is stable for one to two weeks.
2. .1N NaOH
3. Reagent grade acetone

* Composition specified in next section.

4. Chromatography solvents:

   a. For separation of NC & NG;
   Toluene: Petroleum Ether (B.P. 35^{o}-60^{o} C): Ethyl acetate; 12:12:1, and

   b. For identification of propellant grade NC;
   Methyl cellosolve: Ethyl alcohol (95%); 15:85.

5. Chromatography plates:
   Schleicher & Schuell Silica Gel G1500, or equivalent, 250 μm thickness on glass backed plates. Plates are cut to a convenient size such as 10 x 10 cm and are activated by heating for 30 min. at 100^{o} C.

6. Fine-pointed forceps, such as Dumont #5.

7. Small vials or containers with tight lids, such as 1.5 ml Eppendorf centrifuge tubes.

8. Tape for removing particles from hands. The metal disk covered with Scotch 465 transfer tape is suitable.

9. Sprayer-atomizers for spraying NaOH and Saltzman solutions onto plate. The "Chromist" spray unit from Gelman Instrument Co. is suitable.

10. Standard solutions:

   a. Nitroglycerine: .1 mg/ml & .01 mg/ml in acetone, and

   b. Nitrocellulose: 1 mg/ml in acetone.
      Non-propellant: Dupont DHB14P.
      Propellant: Single base smokeless powder from a .357 magnum, Norma, 158 gr RNL cartridge.

11. Optional: Powdered or any other single base powder TLC silica gel, such as EM Silica gel 60 mesh

Procedure

1. Inspect hand for visible smokeless powder flakes using a hand lens. Flakes greater than .1 mm are visible. Using forceps, transfer flakes to vial and seal.

2. Sample the hand in the usual manner, i.e., web, fingers, back of hand and wrist with transfer tape.

3. Transfer flakes from vial to a TLC plate using forceps. Individual flakes are placed separately at the origin. Spot particle twice with 5-10 µl acetone to dissolve flakes. Badly charred or burnt flakes will not dissolve and in general cannot be tested by this procedure.

4. When many (>10) flakes are available, an alternate method for the transfer of collected flakes is to first suspend them in acetone.

   Add 50 µl reagent grade acetone to the vial and mix thoroughly using a vortex mixer. Be certain that flakes are swept off the sides of the vial into the solvent.

   1. Evaporate to about 10 µl by uncapping the vial, and
   2. Put 5 µl of concentrated sample on the plate.

5. Examine the tape under a low power microscope (7-10x). Transfer to the TLC plate any easily removable particles which appear yellowish to yellowish green or pale tan to light brown. These particles are usually of irregular shape. Forceps and a fine pointed probe are suitable transfer tools. Spot the particles twice with 5-10 µl acetone to dissolve.

6. Spot 1µl of each standard on plate.

7. Sequential chromatography:

   Step 1. Chromatograph plate for 2.5 cm in methyl cellosolve: ethanol solvent. Mark front and allow to dry.

   Step 2. Rechromatograph plate for 5.0 cm in toluene: pet ether: ethyl acetate. Mark front and allow to dry.

8. Spray plate lightly but thoroughly with .1N NaOH and immediately dry at 100°C for 6 min. This hydrolyzes NO_2^- groups from parent compound while minimizing diffusion.

9. When cool, spray with Saltzman reagent. The presence of NO_2^- initiates a diazo coupling in the visualizing reagent. Positive reactions are pink and highly concentrated samples have a yellow center with a pink halo.

10. Sensitivity of reagent, lower limit;
    NG - 10 ng/sample
    NC - 500 ng/sample

11. Note presence and position of spots. Allow to dry 1-2 hours away from light. A warm oven at 37°C is suitable although not necessary. The visible reaction spot usually fades as the plate dries.

12. Photograph by contact photography using a high contrast, red-insensitive film such as Kodak Professional Film 7302. An enlarger makes a suitable light source. With the light source distance at 88 cm, and f:11, t = 5 sec.

    The positive reaction spots appear as light spots on the negative and can often be photographed 24 hours after plate visualization even when no longer visible to the eye. It is necessary to protect the plate from light. Once the background turns pink the plate is no longer useful for photography.

Results

Step 1 of the chromatographic procedure distinguishes propellant from non-propellant nitrocellulose. In 15% methycellosolve in ethanol, most of the propellant grade NC remains at the origin with a small amount moving with the solvent front. For non-propellant NC the process is reversed; most of the NC moves with or just behind the solvent front.

Step 2 of the procedure distinguishes NG from non-propellant NC. During Step 1, NG moved with the solvent front along with short chain NC. In toluene: pet ether: EtOAc, NG chromatographs with an R_f of .3 while NC remains stationary.[15]

Rapid Screening Procedure (Optional)

When a rapid screening procedure is desired, the following method can be used if the tape sample is not to be used for additional tests.

1. Dip or dust tape with loose TLC silica gel and lightly tap off excess.
2. Spot surface with 2 μl aliquots of acetone until the entire surface is covered. The silica gel prevents diffusion of low concentrations of NG and/or NC.
3. Spray lightly, (do not wet!) with .1 N NaOH, dry for 6 min. at 100°C, cool, and spray lightly with Saltzman reagent.
4. Examine under a low power microscope for pink areas (positive reaction).

APPENDIX E. DATA TABLES

The tables which comprise this appendix contain the data of interest which has resulted from the field test.

Table 5. Field Test GSR Luminescence Data
Maricopa Medical Examiner's Office, Phoenix, Arizona

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
P-1	Rev., .38, S & W, 4 in.; Reload, bare lead	M/Laborer	12-14	R-back L-back	0.6 1.3	ND[a] 0.3	Outdoors, gun near right hand.
P-2	Auto., .380, F & I, 4 in.; R-P jacketed	F/Housewife	3	R-back L-back	2.4 0.4	0.28 0.09	Indoors, gun near right hand.
P-3	Rifle, .22, Rem 20 in.; Rem short plated	M/Unemployed	10	R-back L-back	0.63 0.07	ND[a] ND[a]	Outdoors, wound right neck.
P-4	Rev., .22, Ruger, single action, 5 1/2 in.; WW Super X Magnum, SJHP	M/Truckdriver	4	R-back L-back	0.24 0.28	ND[a] ND[a]	Indoors, wound behind right ear.
P-5	Rifle, .308, 660, 24 in.; Western, Super	M/Unemployed	5	R-back[b] L-back	0.2[b] 0.4	ND[a] ND[a]	Indoors, victim was right handed.

[a]ND = Not Detectable

[b]Heavy Amount of Blood Present

Table 5. Field Test GSR Luminescence Data (Continued)
Maricopa Medical Examiner's Office, Phoenix, Arizona

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
P-6	Derringer, .22, #913 Frontier, 2 in.; R-P, short RNL.	F/Retired	Unk.	R-back L-back	0.5 0.4	ND[a] ND[a]	Indoors, gun near right hand.
P-7	Rev., .22, RG, 14, 2 in.; LR WW, Super X, L	M/Student	12-18	R-back L-back	0.6 0.37	ND[a] ND[a]	Outdoors, wound left temple.
P-8	Rifle, .22, Ranger, single shot, 26 in.; LR, Fed., Plated	M/Carpenter	16-18	R-back	0.7 0.42	ND[a] ND[a]	Inside pickup cab, wound hard palate
P-9	Rev., .22 Rohm RG, 2 in.; U	F/Housewife	18-20	R-back L-back	1.3 1.6	ND[a] ND[a]	Indoors, victim was left handed
P-10	Auto, .25, Tanfoglio, GT 27, 2 in.; Rem, 50 gr., J	M/Warehouse	3	R-back L-back	0.42 0.26	ND[a] ND[a]	Indoors, murder suicide - 2 shots into wife, 2 shots into himself.

[a]ND = Not Detectable

Table 5. Field Test GSR Luminescence Data (Continued)
Maricopa Medical Examiner's Office, Phoenix, Arizona

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
P-11	Rev., .38, Colt, 2 in.; Western, 158 gr. RNL.	F/Housewife	6	R-back L-back	1.8 4.8	0.05 0.28	Outdoors, gun found in right hand.
P-12	Rev., .22, FIE, 2 in.; LR, WW; RNL.	M/Unknown	3	R-back L-back	0.75 5.4	ND[a] ND[a]	Outdoors, R-H firing, heavy powder smudging left palm.
P-13	Rev., .44 Blackhawk, 5 1/2 in. high vel.	M/Car Salesman	4-5	R-back[b] L-back[c]	.29 4.25	.021 .095	Indoors
P-14	Rev., .22 Schmidt-Ostheim-Rohm, 4 in.; R-P, longrifle RNL	M/--	2	R-back[c]	0.50	ND[a]	R-H firing Indoors
P-15	Rev., .38 Special S & W, 6 in. Fed. .38 special RNL	M/Janitor	10 days	R-back[d] L-back[d]	0.15 4.45	ND[a] 0.50	Indoors

[a]ND = Not Detectable [b]Moderate Amount of Blood Present [c]Slight Amount of Blood Present

[d]No Blood Present

Table 5. Field Test GSR Luminescence Data (Continued)
Maricopa Medical Examiner's Office, Phoenix, Arizona

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
P-16	Auto, .22 Ruger, 4 in.; longrifle plated	M/Butcher	4 1/2	R-back[a] L-back[a]	0.23 0.11	ND[b] ND[b]	R-H Firing Indoors
P-17	Shotgun, 12 Ga. Ithica, 26 in. W-W XL 900 auto. #8 shot	M/Laborer	8-10	R-back[c] L-back[d]	0.14 0.65	ND[b] ND[b]	Indoors
P-18	Shotgun, 12 Ga. Rem., 28 in., Rem. #6 shot	M/Unemployed	--	R-back[d] L-back[c]	0.45 0.88	.02 .07	Indoors

[a]Moderate Amount of Blood Present [b]ND = Not Detectable [c]Slight Amount of Blood Present

[d]No Blood Present

Table 6. Field Test Data (Control Samples)[a]
Maricopa County Medical Examiner's Office, Phoenix, Arizona

Case No.	Victim's Sex & Occupation	Hand Area Sampled	Lead Found μg	Antimony Found μg	Comments
PC-1	F/Housewife	R-back L-back	0.01 0.06	ND[b] ND[b]	Cause of death - heart disease.
PC-2	M/Retired	R-back L-back	0.08 0.05	ND[b] ND[b]	Cause of death - heart disease.
PC-3	F/Housewife	R-back L-Back	0.05 0.04	ND[b] ND[b]	Cause of death - inhalation of auto exhaust.
PC-4	M/Retired	R-back L-back	0.08 0.10	ND[b] < 0.01	Cause of death - internal bleeding.
PC-5	M/Tire Changer	R-back L-back	0.09 0.05	ND[b] ND[b]	
PC-6	M/Consulting Engineer	R-back L-back	0.06 0.04	ND[b] ND[b]	
PC-7	M/Postal Employee	R-back L-back	0.05 0.05	ND[b] ND[b]	Cause of death - diabetes.
PC-8	F/Realtor	R-back L-back	0.01 0.01	ND[b] ND[b]	Died in hospital under sterile conditions.
PC-9	F/Retired	R-back L-back	0.03 0.01	ND[b] ND[b]	History of high blood pressure and hypertension.
PC-10	M/Warehouse worker	R-back L-back	0.55 0.28	ND[b] ND[b]	Cause of death - heart attack. Dirt present on samples.

[a] Analyses of the samples were done by The Aerospace Corporation.

[b] ND = Not Detectable

Table 6. Field Test Data (Control Samples)[a] (Continued)
Maricopa County Medical Examiner's Office, Phoenix, Arizona

Case No.	Victim's Sex & Occupation	Hand Area Sampled	Lead Found µg	Antimony Found µg	Comments
PC-11	F/Housewife	R-back L-back	0.06 0.04	ND[b] ND[b]	Cause of death - hung herself.
PC-12	F/Housewife	R-back L-back	0.03 0.07	ND[b] < 0.01	Cause of death - tube pregnancy.
PC-13	F/Housewife	R-back L-back	0.48 0.92	ND[b] ND[b]	Cause of death - victim was struck and run over by an automobile. Moderate amount of dirt present on samples.
PC-14	M/Student	R-back L-back	0.05 0.05	ND[b] ND[b]	History of heart trouble. Slight amount of dirt present on samples.
PC-15	M/Bartender	R-back L-back	0.04 0.03	ND[b] ND[b]	Cause of death - victim was struck by an automobile.
PC-16	M/Retired	R-back L-back	0.15 0.05	ND[b] ND[b]	History of heart trouble. Dirt present on samples.

[a] Analyses of the samples were done at The Aerospace Corporation.

[b] ND = Not Detectable

CONTINUED

1 OF 2

Table 7. Field Test GSR Luminescence Data
Southwestern Institute of Forensic Sciences, Dallas, Texas

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found(μg) (blood in solution)	Antimony Found (μg)	Comments
D-31	Rev., .38, S & W, Spl., --; R-P, HP	F/--	--	R-back[a] R-palm[a] L-back[a] L-Palm[a]	2.08 0.24 0.15 0.25	0.14 0.01 0.002 ND[b]	Indoors wound on right side of head
D-32	Auto., .32, --, --; --	F/--	--	R-back[a] R-palm[a] L-back[c] L-palm[c]	0.20[a] 0.05[a] 0.04[a] 0.03[a]	0.02 0.006 ND[b] ND[b]	Indoors, wound on right side of head
D-33	Rifle, .22, Winch, M-67, --; R-P	M/--	--	R-back[c] R-palm[c] L-back[c] L-palm[c]	0.42[c] 0.10[c] 0.19[c] 0.83[c]	ND[b] ND[b] 0.006 0.005	Indoors
D-34	Shotgun, 16G, Revelation, --; W-W	M/--	--	R-back[c] R-palm[c] L-back[c] L-palm[c]	0.12[c] 0.10[c] 0.13[c] 0.12[c]	ND[b] ND[b] ND[b] ND[b]	Indoors
D-35	Rev., .38, S & W, Spl., M-10, --; W-W, RNL	M/--	--	R-back[d] R-palm[a] L-back[e] L-palm[e]	0.49[c] 0.15[a] 0.90[a] 1.22[a]	0.11 ND[b] 0.034 0.006	Indoors
D-36	Rifle, .22, --, --, --, --; RP, RNL	M/--	--	R-back[c] R-palm[a] L-back[a] L-palm[a]	0.23[a] 0.08 0.05 0.05	ND[b] ND[b] ND[b] ND[b]	

[a]No Blood Present [b]Not Detectable [c]Slight Amount of Blood Present

[d]Heavy Amount of Blood Present [e]Moderate Amount of Blood Present

Table 7. Field Test GSR Luminescence Data (Continued)
Southwestern Institute of Forensic Sciences, Dallas, Texas

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
D-37	Rev., .38, S & W, Spl., --; SV, RNL	F/--	--	R-back[a] R-palm[a] L-back[a] L-palm[a]	1.21[b] 0.13[b] 0.50[b] 0.08[b]	0.10 ND[c] 0.006 ND[c]	Indoors
D-38	Rev., .22, R.G, --, --; RP, RNL	F/--	--	R-back[b] R-palm[d] L-back[b] L-palm[b]	0.20 0.13[b] 0.19 0.23	ND[c] ND[c] ND[c] ND[c]	Outdoors
D-39	Rifle, --, --, --, --; --, --	M/--	--	R-back[d] R-palm[d] L-back[a] L-palm[e]	0.20[b] 0.14[b] 0.10[d] 0.01[d]	ND[c] ND[c] ND[c] ND[c]	Outdoors; Identified as a homicide
D-40	Rev, .32, A.C.P., --, --, --; RP, FMJ	M/--	--	R-back[a] R-palm[a] L-back[e] L-Palm[a]	0.09[d] 0.13[d] 0.05[e] 0.08[d]	ND[c] ND[c] ND[c] 0.018	Outdoors; Identified as a homicide

[a]Moderate Amount of Blood Present [b]No Blood Present [c]Not Detectable

[d]Slight Amount of Blood Present [e]Heavy Amount of Blood Present

NOTE:

Data from cases D-1 through D-30 could not be used due to instrumental problems during analyses.

Table 8. Field Test Data
Georgia State Crime Laboratory, Atlanta, Georgia

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
A-1	Rev., .38, Colt, 2 in.; Peters, RNL	M/--	1	R-back	1.85	ND[a]	Indoors
A-2	Rev., .38, Charter Arms Speer, --, --	--/--	--	--	4.55	0.2	
A-3	Rev., .22, RG Remington, --, --	--/--	--	R-back R-wrist L-back L-wrist	0.3 0.20 0.05 0.28	ND[a] ND[a] ND[a] .002	
A-4	--	--/--	--	--	1.65	ND[a]	
A-5	Rev., .38, S & W, --; --	--/--	--	--	0.35	ND[a]	
A-6	Rev., .32, S & W, 4 in.; RP	M/Unemployed	5	R-back	1.55	ND[a]	Indoors
A-7	Rev., .38, Taurus, 4 in., WW, J	M/--	1 1/2	R-back	0.25	ND[a]	Indoors

[a]Not Detectable

Table 8. Field Test Data (Continued)
Georgia State Crime Laboratory, Atlanta, Georgia

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
A-8	Rev., .357, S & W, 2 in.; SJHP	M/Police Lt.	3	R-back	3.2	ND[a]	Indoors
A-9	Rev., .38, INA, 1 1/2 in., REM. RNL	M/Paint Salesman	4	R-back	0.65	ND[a]	Indoors
A-10	Shotgun, .410, Sears, 26 in.; #5 shot	M/--	3-4	R-back L-back	0.8 0.35	ND[a] ND[a]	Outdoors
A-11	Rev., .45, Colt U.S. Army, 4 in., Peters ACP, J	F/Unknown	1	R-back R-wrist	0.15 0.15	ND[a] ND[a]	Indoors

[a]Not Detectable

Table 9. Field Test Data (Control Samples)[a]
Georgia State Crime Laboratory, Atlanta, Georgia

Case No.	Victim's Sex & Occupation	Hand Area Sampled	Lead Found µg	Antimony Found µg	Comments
AC-1	F/Housewife	L hand	0.10	ND[b]	
AC-2	F/Housewife	--	0.06	ND[b]	
AC-3	--/Secretary	--	0.07	< 0.01	
AC-4	--/Nurse	--	0.35	< 0.01	
AC-5	--/Photographer	--	0.13	ND[b]	

[a]Analyses of the samples were done by The Aerospace Corporation

[b]Not Detectable

Table 10. Field Test Data
Office of the Chief Medical Examiner, Baltimore, Maryland

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found(μg) (blood in solution)	Antimony Found (μg)	Comments
B-1	Rev., .22, 2 in.; short, plated	M/Student	19	R-back & wrist [b]	0.4	ND [a]	Indoors
B-2	Rev., .38, S & W, 2 in.; L	M/Accountant	27	R-back & wrist [c]	0.75	ND [a]	Outdoors, shot wife four times, self once.
B-3	Shotgun, 12 G, Rem., 36 in.; Rem., #7 lead Shot	M/Unemployed	13 1/2	R-back & wrist [c]	ND [a]	ND [a]	Indoors
B-4	Auto, .25, 2 in.; SJL	M/Retired	23+	R-back & wrist [d] L-back [e]	ND [a] 0.9	ND [a] .01	Indoors
B-5	Rev., .22, --; SJL	F/Housewife	24	R-back [c] L-back [e]	0.3 0.6	.003 .006	Indoors
B-6	Rev., .38, H & R, 2 1/2 in.; L	F/Housewife	21	R-back & wrist [c] L-back [e]	1.2 0.9	.014 .008	Indoors, 2 shots
B-7	Shotgun, 12 G, Win., 36 in.; Rem., #7 lead shot	M/Unknown	12-14	R-back [c] L-back [c]	0.35 0.25	.005 .007	Indoors

[a] Not Detectable [b] Moderate Amount of Blood Present [c] Slight Amount of Blood Present

[d] Heavy Amount of Blood Present [e] No Blood Present

Table 10. Field Test Data (Continued)
Office of the Chief Medical Examiner, Baltimore, Maryland

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
B-8	Rev., .38, S & W, 4 in.; U	M/Farmer	20	R-back[a]	0.2	.003	Indoors
B-9	Rev., .22, -- 2 in.; long, L	M/Factory worker	11	R-back[a]	.25	.003	Indoors
B-10	Rev., .38, S S & W, 2 in.; L	M/Restaurant Owner	24	R-back[b]	ND[c]	ND[c]	Indoors
B-11	Rifle, .22, Rem., SS; plated	M/Unknown	5 1/2	R-back[a]	ND[c]	ND[c]	Indoors
B-12	Auto, .25, 2 in.; Std., FJ	M/Gov't. Employee	14-15	R-back & wrist[a]	.07	ND[c]	Indoors
B-13	Rev., .38, Colt, 2 in.; Std., L	M/--	12	R-back & wrist[a]	0.63	ND[c]	Indoors
B-14	Shotgun, 16G, Rem., 36 in.; Std.	M/Student	13-14	R-back & wrist[a]	0.14	.005	Indoors
B-15	Rifle, .30, Marlin; BL	M/Gas station attendant	14	R-back & wrist[d]	.05[a]	.006	Outdoors

[a]No Blood Present [b]Heavy Amount of Blood Present [c]Not Detectable [d]Slight Amount of Blood Present

Table 11. Field Test Data (Control Samples)[a]
Office of the Chief Medical Examiner, Baltimore, Maryland

Case No.	Victim's Sex & Occupation	Hand Area Sampled	Lead Found µg	Antimony Found µg	Comments
BC-1	F/Housewife	R-hand	0.13	ND[b]	Cause of death - cardio-vascular disease.
BC-2	M/Garbage Collector	R-hand	0.15	ND[b]	Cause of death - stab wounds. Slight amount of blood present on samples.
BC-3	M/Unknown	R-hand	0.25	ND[b]	Cause of death - cardio-vascular disease. Slight amount of dirt present on samples.
BC-4	M/Retired Laborer	R-hand	0.18	ND[b]	Cause of death - cardio-vascular disease.
BC-5	M/Unknown	R-hand	0.15	ND[b]	Cause of death - trauma. Slight amount of dirt present on samples.
BC-6	M/Accountant	R-hand	0.28	ND[b]	Cause of death-cardio-vascular disease. Slight amount of dirt present on samples.
BC-7	M/Heavy Equipment Operator	R-hand	0.35	ND[b]	Cause of death - trauma. Slight amount of dirt present on samples.
BC-8	F/Housewife	R-hand	0.09	ND[b]	Cause of death - overdose. Slight amount of dirt present on samples.
BC-9	M/Student	R-hand	0.03	ND[b]	Cause of death - trauma. Slight amount of dirt present on samples.
BC-10	M/Photographer	--	0.05	ND[b]	
BC-11	M/Maintenance Man	--	0.05	ND[b]	
BC-12	M/Morgue Attendant	--	0.11	ND[b]	

[a]The samples were analyzed by The Aerospace Corporation

[b]Not Detectable

Table 12. Field Test GSR Luminescence Data
Department of the Chief Medical Examiner/Coroner, Los Angeles, California

Case No.	Weapon, Barrel Length, and Ammunition	Victim's Sex & Occupation	Hrs Between Firing and Sampling	Hand Area Sampled (blood on disk)	Lead Found (μg) (blood in solution)	Antimony Found (μg)	Comments
L-1	Rev., .22, Ruger, 4 in.; 40 gr.	M/Unemployed	--	R-back[a] L-back[a]	0.1 0.46	0.034 0.056	Indoors
L-2	Rev., .22, High Std., 6 in.; W-W, Super X, L	M/Unemployed	2	R-back[a] L-back[a]	0.7 0.5	0.032 0.026	Outdoors
L-3	Rev., .22, Ruger, Single Six, 4 in., LR, Rem., L	M/--	6	R-back[a] L-back	0.32 0.45	0.026 0.014	Indoors
L-4	Rev., .38, Colt, 2 in., R-P, 158 gr., SJ	M/--	--	R-back L-back	2.84 0.84	0.158 0.046	Indoors, weapon found in right hand.
L-5	Rev., .38, S & W., 6 in., Rem., 158 gr., SJ	M/Plumber	2	R-back[a] L-back[a]	0.47 0.2	0.10 0.38	Indoors
L-6	Auto, .25, Eibar., U	M/--	--	R-back[b] L-back[a]	0.76 0.77	0.048 0.021	Indoors

[a]Moderate Amount of Blood Present [b]Slight Amount of Blood Present

Table 12. Field Test GSR Luminescence Data (Continued)
Department of the Chief Medical Examiner/Coroner, Los Angeles, California

Case No.	Weapon, Barrel Length; and Ammunition	Victim's Sex & Occupation	Hours Between Firing and Sampling	Hand Area Sampled (Blood on Disk)	Lead Found (μg) (Blood in Solution)	Antimony Found (μg)	Comments
L-13	Auto, .45, Ruger, Blackhawk, 6 in., L	M/Writer	--	R-back[a] L-back	1.79 0.53	0.038 0.027	Indoors
L-14	Rev., .357 Mag., Ruger, Blackhawk, 4 1/2 in., Win., Super, LHP	M/--	2	R-back L-back[b]	0.12 0.18	0.048 0.050	Outdoors, dirty hands
L-15	.22, 2 in., short, plated	M/Clerk Foreman	2	R-back[a] L-back[a]	0.74 0.16	0.032 0.026	Indoors, 2 shots

[a]Moderate Amount of Blood Present [b]Slight Amount of Blood Present

Table 12. Field Test GSR Luminescence Data (Continued)
Department of the Chief Medical Examiner/Coroner, Los Angeles, California

Case No.	Weapon, Barrel Length; and Ammunition	Victim's Sex & Occupation	Hours Between Firing and Sampling	Hand Area Sampled (Blood on Disk)	Lead Found (μg) (Blood in Solution)	Antimony Found (μg)	Comments
L-7	Rev., .22, 6 in., L	M/--	3 1/2	R-back L-back	0.52 0.57	0.014 0.034	Indoors
L-8	Shotgun, .410, savage, 220A, 36 in., U	M/Diesel Mech.	3	R-back[a] L-back[a]	0.24 0.24	0.012 0.012	Indoors
L-9	Shotgun, 16 G, Stevens, 30 in., Western, Super X, 7 1/2 shot	M/Ret. Col.	7	R-back[a] L-back[a]	0.96 0.97	0.032 0.046	Indoors
L-10	Rifle, .22, Marlin, 989 M-2, 18 in., CCI, SJ	M/Oil Field Maintenance	--	R-back L-back	0.52 0.34	.018 .01	Indoors, dirty hands
L-11	Rev., .22, H & R, 949, 6 in., Western, Super X, long, SJ.	M/Tree Trimmer	5	R-back L-back	0.76 0.42	0.039 0.014	Indoors
L-12	Rev., .22, H & R, 949, 6 in., Western, Super X, SJ	F/Housewife	5	R-back L-back[a]	0.63 0.42	0.021 0.013	Indoors

[a]Moderate Amount of Blood Present

Table 13. Field Test Data (Control Samples)[a]
Department of the Chief Medical Examiner/Coroner, Los Angeles, California

Case No.	Victim's Sex & Occupation	Hand Area Sampled	Lead Found (μg)	Antimony Found (μg)	Comments
LC-1	M/Unemployed	R-back L-back	0.46 0.52	ND[b] ND	
LC-2	M/--	R-back L-back	1.68 1.04	ND ND	Cause of death - overdose. Dirt and paint present on samples.
LC-3	M/Warehouse Foreman	R-back L-back	0.54 0.70	ND ND	Cause of death - heart attack.
LC-4	F/Unknown	R-back L-back	0.81 0.72	ND ND	Cause of death - fatal jump from hotel.
LC-5	M/Unknown	R-back L-back	0.22 0.36	ND ND	Cause of death - stab wounds. Blood present on samples.
LC-6	F/Unknown	R-back L-back	0.334 0.336	$\leq$ 0.052 $\leq$ 0.021	
LC-7	M/Helicopter Pilot	R-back L-back	0.105 0.160	$\leq$ 0.013 $\leq$ 0.096	Cause of death - helicopter collision. Blood and dirt present on samples.
LC-8	M/Unknown	R-back L-back	0.44 1.30	$\leq$ 0.119 $\leq$ 0.04	Cause of death - fatal jump from hotel. Slight amount of blood present on samples. Some ash-like material?

[a]Samples LC-1 through LC-5 were analyzed by The Aerospace Corporation

[b]Not Detectable

APPENDIX F. OCCUPATIONAL HANDBLANKS

Appendix F is comprised of Table 14, which lists fifty-five handblank samples along with information of interest in this study.

Table 14. Occupational Handblanks

Sample Number	Occupation	Hand	Pb Found (μg)	Sb Found (μg)	Sample Number	Occupation	Hand	Pb Found (μg)	Sb Found (μg)
OHB-1	Secretary	R	0.10	ND[a]					
OHB-2		L	0.15	ND	OHB-30	Lead Foil Manufacturer[b]	R	4.05	ND
OHB-3	Secretary	R	0.18	ND	OHB-31		L	3.73	ND
OHB-4		L	<0.01	ND	OHB-32	Brake Mechanic	R	0.08	ND
OHB-5	Secretary	R	0.10	ND	OHB-33		L	0.23	ND
OHB-6		L	0.13	ND	OHB-34	Brake Mechanic	R	0.10	ND
OHB-7	Electrician[b]	L	0.22	0.001	OHB-35		L	0.18	ND
OHB-8	Painter[b]	R	0.17	0.040	OHB-36	Gas Station Attendant[b]	R	2.15	0.083
OHB-9		L	0.20	ND	OHB-37		L	2.53	ND
OHB-10	Carpenter[b]	R	0.33	0.012	OHB-38	Painter	R	2.53	0.002
OHB-11		L	0.35	0.009	OHB-39		L	2.83	ND
OHB-12	Carpenter[b]	R	0.40	ND	OHB-40	Painter	R	2.60	ND
OHB-13		L	0.25	ND	OHB-41		L	2.35	ND
OHB-14	Electrician[b]	R	0.50	ND	OHB-42	Printer	R	2.55	0.150
OHB-15	Photo technician	R	0.20	ND	OHB-43		L	2.60	0.199
OHB-16		L	0.25	ND	OHB-44	Welder[b]	R	0.85	ND
OHB-17	Machinist	R	0.85	ND	OHB-45		L	0.65	ND
OHB-18		L	0.85	ND	OHB-46	Assembler/Wire Stripper[b]	R	0.33	ND
OHB-19	Machinist[b]	R	0.15	ND	OHB-47		L	0.18	ND
OHB-20		L	0.13	ND	OHB-48	Assembler/Solderer	R	1.30	0.052
OHB-21	Composites Technician	L	0.53	ND	OHB-49		L	1.30	0.063
OHB-22	Machinist	R	0.55	ND	OHB-50	Die Caster[b]	R	0.30	ND
OHB-23	Machinist	R	0.85	ND	OHB-51		L	0.38	ND
OHB-24	Machinist	L	0.45	ND	OHB-52	Die Caster[b]	R	0.30	ND
OHB-25	Painter[b]	L	0.70	ND	OHB-53		L	0.48	ND
OHB-26	Air Conditioning Mech	R	0.33	0.001	OHB-54	Gardener[b]	R	0.60	0.003
OHB-27		L	0.50	0.001	OHB-55		L	0.33	ND
OHB-28	Plumber[b]	R	0.33	ND					
OHB-29		L	0.35	0.003					

[a]Not Detectable [b]Smoker ND = Not Detectable

REFERENCES
(LITERATURE CITED)

1. J. E. Wessel, P. F. Jones, Q. Y. Kwan, R. S. Nesbitt, and E. J. Rattin, "Gunshot Residue Detection, Survey, Assessment, and Identification of Alternate Concepts," The Aerospace Corporation Report No. ATR-75(7915)-1, September 1974.
2. P. F. Jones and R. S. Nesbitt, "A Photoluminescence Technique for Detection of Gunshot Residue," J. Forensic Sciences 20, pp. 231-242, 1975 (Originally published as The Aerospace Corporation Report No. ATR-74(7915)-1, June 1974).
3. R. S. Nesbitt, J. E. Wessel, G. M. Wolten, and P. F. Jones, "Evaluation of a Photoluminescence Technique for the Detection of Gunshot Residue," J. Forensic Sciences 22, pp. 288-303, 1977 (Originally published as The Aerospace Corporation Report No. ATR-76(7915)-1, September 1975).
4. G. M. Wolten, R. S. Nesbitt, A. R. Calloway, G. L. Loper, and P. F. Jones, "Final Report on Particle Analysis for Gunshot Residue Detection," The Aerospace Corporation Report No. ATR-77(7915)-3, September 1977.
5. M. H. Mach, A. Pallos, and P. F. Jones, "Feasibility of Gunshot Residue Detection via its Organic Constituents," The Aerospace Corporation Report No. ATR-77(7915)-1, April 1977.
6. M. E. Cowan, and P. L. Purdon, "A Study of the Paraffin Test," Journal of Forensic Sciences, Vol. 12, 1967, pp. 19-36.
7. H. C. Harrison, and R. Gilroy, "Firearms Discharge Residues," Journal of Forensic Sciences, Vol. 4, 1959, pp. 185-199.
8. H. L. Schlesinger, H. R. Lukens, V. P. Guinn, R. P. Hackleman, and R. F. Korts, "Special Report on Gunshot Residues Measured by Neutron Activation Analysis," Gulf General Atomic, Inc., Report No. GA-9829 (TID-4500), 10 August 1970.

9. G. D. Renshaw, C. A. Pounds, and E. F. Pearson, "Quantitative Estimation of Lead, Antimony, and Barium in Gunshot Residues by Non-Flame Atomic Absorption Spectrophotometry," Atomic Absorption Newsletter, Vol. 12, 1973, pp. 55-56.

10. E. A. Solov'ev, and E. A. Bozhevol'nov, "Low Temperature Luminescent Method for the Determination of Microgram Amounts of Inorganic Impurities," Zhurnal Analiticheskoy Khimii, Vol. 27, 1972, pp. 1817-1827.

11. G. F. Kirkbright, C. G. Saw, and T. S. West, "Fluorescence Characteristics of Inorganic Complexes in Hydrochloric Acid Medium at Liquid-Nitrogen Temperature," Talanta, Vol. 16, 1969, pp. 65-73.

12. W. D. Kinard, and C. R. Midkiff, Jr., "The Application of Oxygen Plasma Ashing to Gunshot Residue Analysis," Paper presented at the 1977 Annual Meeting American Academy of Forensic Sciences, San Diego, Calif., Feb. 15-19, 1977. To be published in the Journal of Forensic Sciences.

13. M. S. Taylor, R. L. Taylor, and T. T. Noguchi, Department of the Chief Medical Examiner-Coroner, County of Los Angeles, California, Paper to be Presented at the 30th Annual Meeting of the American Academy of Forensic Sciences, St. Louis Missouri, February 20, 1978.

14. B. E. Saltzman, et. al., Health Laboratory Science, 6(2), 1969, pp. 10-13.

15. J. D. Twibell, CRE Report 167, Home Office of Central Research Establishment, Aldermaston, 1975.

GLOSSARY

ATF	Bureau of Alcohol, Tobacco, and Firearms
Ba	barium
cm	centimeter
Dewar	vacuum flask, similar to a thermos bottle, that provides a high degree of thermal insulation for the content, which is commonly a cryogenic fluid such as liquid nitrogen
g	gram
gr	grain: bullet weight is given in grains; 1 gr = 0.0648 grams
Handblank	specimen taken from the back of the hand of a person who has not fired a gun
Handsample	specimen taken from the back of the hand
HCl	hydrochloric acid
K	Kelvin
ml	milliliter
mm	millimeter
Monochromator	wavelength selector for the ultraviolet, visible, or infrared spectrum consisting of mirrors and a grating or prism
nm	nanometer: a unit of length equal to 10^{-7} cm that is commonly used in the measurement of light wavelength
Pb	lead
Photoluminescence	light emitted by a chemical species in the visible or ultraviolet wavelength region of the electromagnetic spectrum when the species has been excited with radiation of higher energy
Photomultiplier	an extremely sensitive instrument, which is used for the detection of light, that consists of a photocathode, an anode, and a series of electron multiplier dynodes
Sb	antimony
SEM	Scanning Electron Microscope
μg	microgram: one millionth of a gram (10^{-6} g)

END