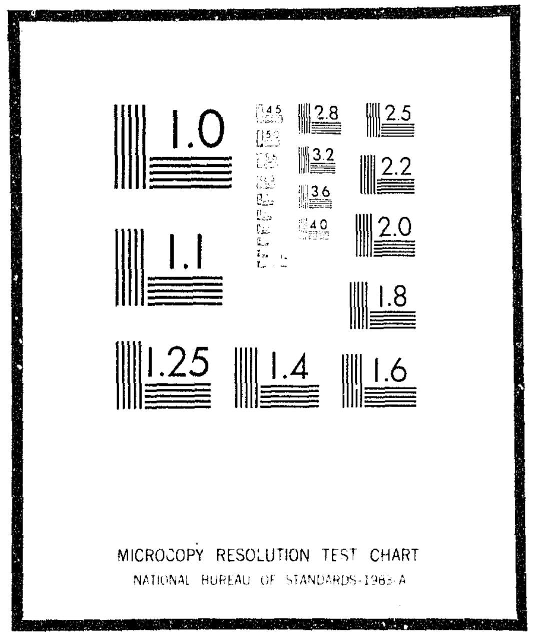

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EQUIPMENT SYSTEMS IMPROVEMENT PROGRAM

CONCLUSIVE DETECTION OF GUNSHOT RESIDUE BY THE USE OF PARTICLE ANALYSIS

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Approved

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ABSTRACT

The scanning electron microscope with energy-dispersive X-ray fluorescence detection has been used to provide highly reliable identification of gunshot residue particles. The residue particles deposited on the hand were examined for morphological characteristics and elemental composition. They can be classified in terms of three categories:

- Partially burned fragments of smokeless powder that range from 10^{-2} to 10^{-1} cm in diameter. These particles have a highly distinctive appearance and are covered with small spheres that contain combinations of lead, barium, and antimony.
- Particles of spherical or distorted spherical shape that range from 3×10^{-4} to 6×10^{-3} cm. These particles contain combinations of lead, barium, and antimony.
- Nondescript particles that range from 5×10^{-4} to 5×10^{-2} cm. These contain combinations of lead, barium, and antimony.

The combination of morphological and elemental information is adequate to permit reliable identification of residue handsamples. A set of randomly mixed "unknown" specimens was formed from 15 firing handsample specimens and 16 handblank specimens that had been collected rapidly and easily by pressing an adhesive layer attached to aluminum blocks against the hand surface. In a blind test, the analyst was able to correctly identify each aluminum block, frequently within 10 min time. Since one-half of the firing specimens were from .22 caliber handgun firings, which

are difficult to detect by other methods, and one-half of the handblanks were from individuals with high exposure to contaminant particles, the 100% success of identification by use of the scanning electron microscope is a major improvement over current methods of residue detection.

SUMMARY

Detection of gunshot residue on the hand of a person suspected of having fired a gun is potentially one of the most important criminalistic techniques. The best methods of detection being used are not satisfactory to criminalists because they do not provide the required high rate of successful identification of firing specimens inasmuch as they measure only the total quantity of the elements characteristic of residue — lead, barium, and antimony. This provides less information than is desired since these elements also occur in the environment and therefore can be present in handblanks.

In this investigation, the use of the scanning electron microscope (SEM) for residue identification has been explored because it offers the possibility of increasing the capability to identify residue specifically by combining morphological information with elemental analysis of each individual particle. The SEM technique is particularly attractive because specimen preparation, analysis, and data evaluation are reasonably easy for a trained operator, and the instrumentation is currently available in some criminalistics laboratories and could be provided by regional laboratories. Examination of pure residue particles from a group of six handguns representative of those encountered in criminalistic work resulted in formulation of three convenient particle classifications:

- Partially burned fragments of smokeless powder particles that range from 10^{-2} to 10^{-1} cm in diameter. These are frequently encountered in residues from semiautomatic pistols and in the muzzle discharge of all guns, but not in residue deposited on

the hand by new revolvers of high quality. The particle shapes are highly distinctive, being smoothly contoured with holes and craters that penetrate the surfaces. Nearly spherical globules are randomly sprinkled over the surfaces of these particles, and the spheres appear bright in the SEM micrographs. The substrate particle contains little lead, barium, or antimony (and is composed primarily of organic material), whereas the spherical particles contain high concentrations of lead, barium, or antimony, or combinations thereof.

- Spherical particles of from 3×10^{-4} to 6×10^{-3} cm in diameter. These are common among the isolated particles of the residue as well as on the surface of larger particles of partially burned smokeless powder. Their shape, taken together with elemental content, provides an easily identifiable feature common to residue. They are believed to be formed from condensation of bullet and spent primer constituents, and their small size is consistent with the fact that they are ejected through the small gaps between the cylinder and barrel of a gun.
- Particles of nondescript morphology that range from 5×10^{-4} to 5×10^{-2} cm. These are also common in residue, and they contain lead, barium, or antimony, or combinations thereof. They are not readily identified on the basis of shape alone and can resemble environmental particles.

Most particles examined from handblanks have had morphologies and elemental content quite distinct from gunshot residue. A large fraction of environmental particles on the hand are of mineral origin, have crystalline features, and produce calcium and silicon X-ray fluorescence. Dermal particles are commonly encountered. These particles have distinctive appearance and produce only a broad background of X rays rather than fluorescence because of their organic chemical composition. Particles that contain lead (such as from automobile exhaust emission) also contain such other identifying elements as bromine, and, therefore, can be distinguished from the nondescript particles of gunshot residue.

A "blind" test was conducted to investigate the feasibility of identification of residue in actual handsamples. A randomly mixed sample of 15 handblanks and 16 firing specimens was subjected to SEM examination for the presence of residue. Each specimen was identified correctly, even though the SEM analyst was not aware of the identity of specimens. The firing handsamples included eight firings of .22 caliber guns, and the handblanks included nine samples from individuals with high exposure to contaminants. For the conventional elemental analysis methods, a large number of incorrect determinations would be expected in this sampling. Thus, the SEM procedure is a major improvement in capability. However, before it can be considered as an established method, standard analysis procedures must be defined, the ability to detect residue collected a significant time after firing must be established, and the possibility of using the vast amount of additional information made available by the technique for other criminalistic purposes should be investigated. It might be possible to distinguish between the different guns and ammunition by residue analysis and to distinguish between residue deposited on the firing hand and that deposited on bystanders.

The method is more expensive in instrumentation (up to $50,000) and operator cost (up to one hour per specimen) than some of the recent chemical analysis techniques such as flameless atomic absorption and molecular luminescence spectroscopy. Therefore, it is not well suited to the small criminalistics laboratory. The preferred operational mode is to furnish SEM analysis at the regional laboratory level as a service for local laboratories. This approach would require the local laboratories to use a screening technique, such as atomic absorption or molecular luminescence spectroscopy, for potentially positive specimens and then send out only the positive samples for SEM analysis. The SEM micrographs of residue particles, which a jury should find particularly meaningful as court evidence, would be made available at the time of a trial.

CHAPTER I. INTRODUCTION

The unambiguous identification of gunshot residue on the hand of a person suspected of having fired a gun can provide extremely important evidence for investigative and court use. The most reliable methods currently used to determine if a suspect has fired a gun rely on measurements of the quantities of antimony, barium, and lead on the hand. This procedure is based on the presence of these elements in the primer of the ammunition together with the tendency of ammunition combustion products to vent from the firing chamber in various directions, including toward the hand. The mere presence of these metals on the hand is not conclusive proof of the presence of residue because the elements are encountered in the environment. In fact, if a threshold level is set for quantities of these elements above which there is low probability that the measurement is consistent with a handblank (no firing), then there are few positive analyses even for controlled test firings from small guns or for detection several hours after firing.

An effort has been undertaken to apply the SEM and particle analysis technique to improve the capability to detect gunshot residue on the hand. During the past decade, the SEM has become a powerful and widely used analytical instrument. By combining an X-ray detector with the instrument, simultaneous information on morphology and elemental content is readily obtained. The ease of operation made possible by the ability to analyze nonuniform, thick specimens without elaborate sample preparation has resulted in extensive and routine use of this type of instrument. Its high resolution

(10^{-6} cm) and great depth of field can be of considerable value in forensic work. Criminalistic applications of the SEM have been reviewed in a series of articles.[1-11] In one of these studies,[11] photomicrographs of gunshot residue particles on cloth were presented.

By combining the geometrical information about the shape of a gunshot residue particle with the elemental analysis of the individual particles, it is possible to draw a much firmer conclusion as to the source of the particle, viz., gunshot residue versus an environmental particle. Since lead styphnate is the major component of most contemporary primers (typical primer formulations are given in Table 1), and lead is abundant in most bullets, it is anticipated that residue particles will be rich in lead. Barium and antimony also occur in many primers, and antimony is alloyed with the lead to harden bullets; therefore, these elements are also anticipated. The results of extensive studies of residue particles and analyses of numerous handsamples are presented here. The basic objective of this investigation was to improve the rate of success in identification of residue particles by using the newly available capability of the SEM. The elemental analysis procedures currently used for residue detection (neutron activation and atomic absorption) have provided fewer than 10% conclusive analyses in practice, primarily because of the moderately high environmental background of antimony, barium, and lead.[12] Through this study, it has become apparent that major improvements can be made and that the new technique is moderately rapid when performed by a trained microscopist. Although the equipment is complex and expensive for the typical criminalistics laboratory, it is less expensive, and analysis is much simpler, than neutron activation analysis, which has been the preferred method until the recent introduction of atomic absorption spectroscopy. Atomic absorption provides the average criminalistics laboratory with detection capability, but does not substantially improve the number of conclusive results.

Table 1. Typical Chemical Compositions of Handgun Priming Mixtures used in the U.S.

Component	Composition, %				
	1	2	3	4	5
Lead styphnate	36	41	39	43	37
Barium nitrate	29	39	40	36	38
Antimony sulfide	9	9	11		11
Calcium silicide		8		12	
Lead dioxide	9				
Tetrazene	3	3	4	3	3
Zirconium	9				
Pentaerythritol tetranitrate	5				5
Nitrocellulose			6		
Lead peroxide				6	6

In addition to a requirement for improved analysis procedures, successful detection of gunshot residue requires a method of residue collection and specimen preparation that is simple and reliable. Ideally, the sample collection will preserve information about the spatial distribution of residue, which can provide additional criminalistics information.[13,14] The material used for collection must be storable before and after specimen collection, and it cannot introduce impurities that interfere with analysis.

In past work, the collection methods have been developed primarily for bulk elemental analysis methods. For example, paraffin and plastic film casts have been used to collect specimens for color tests and neutron activation analyses, and cotton swabs are used extensively for neutron activation and atomic absorption analyses. None of these appear readily adaptable to SEM analysis, which requires that the particulate matter be retained on the surface of a collection material.

CHAPTER II. BACKGROUND AND RELATED WORK

The basic physical and chemical forms of gunshot residue particles have not been well characterized. It is generally accepted that most handguns produce residue deposits that contain visible particles that range from 0.01 to 0.1 cm, plus smoke deposits, and there is unanimous agreement that there is a wide variation in the properties of residue produced by different firings of a single gun under uniform conditions.[13,15-17] In earlier investigations, considerable attention was given to the detection of nitrates and nitrites in the large particles found on the hand after discharge of a gun.[18] Not all guns deposited these particles. Attention was directed later to the inorganic elements, and in reports of the Gulf General Atomic group[13] and the Aldermaston group,[17] it was concluded that most of the antimony and barium in residue on the hand is contained in a few large particles.[13] Some attention has been given to elemental characterization of individual residue particles by autoradiography[17, 19, 20] and by chemical color tests.[21] These studies have shown that individual visible particles do indeed contain characteristic heavy metals.

The most extensive published autoradiography studies relating to the specific nature of residue deposits are those of Gislason and Pate,[19] who studied residue deposits issuing in various directions from a gun. In this work, three types of residue were revealed by autoradiography after neutron activation: (1) a fine smoke deposit, (2) radioactive spots corresponding to visible spots, and (3) similar spots that were not visible to the naked eye.

All were found to contain a diverse and variable assortment of the heavy metals expected on the basis of primer composition. No detailed data acquired using this technique were available on the nature of chemical compounds in the smoke deposit. Similar studies of residue deposits by Bashinski[21] using the sodium rhodizonate test have clearly demonstrated the presence of lead in both large particles and smoke deposits. Some of this work can be best interpreted on the basis of the bullet as a primary source of residue lead. The study of Renfro and Jester[22] provided information that indicated that the cloud of residue produces a diverse range of particle sizes. They studied the residue suspended in the air of a room following firing as a function of time between firing and air sampling. The large particles settle rapidly onto surfaces, but smaller particles, which contain substantial antimony and barium, remain suspended for appreciable periods, some for as long as a day. These are presumably submicron-size particles. Another source of information are the data presented by Stiefel and Brodman[23] on the composition of M16 rifle fouling residues. They analyzed material that collected in various portions of the rifle and found that organic and inorganic solids collect in abundance, particularly if certain compounds, such as calcium carbonate, have been incorporated in the propellant. The composition of muzzle smoke from rifles has been investigated by several laboratories.[24-26]

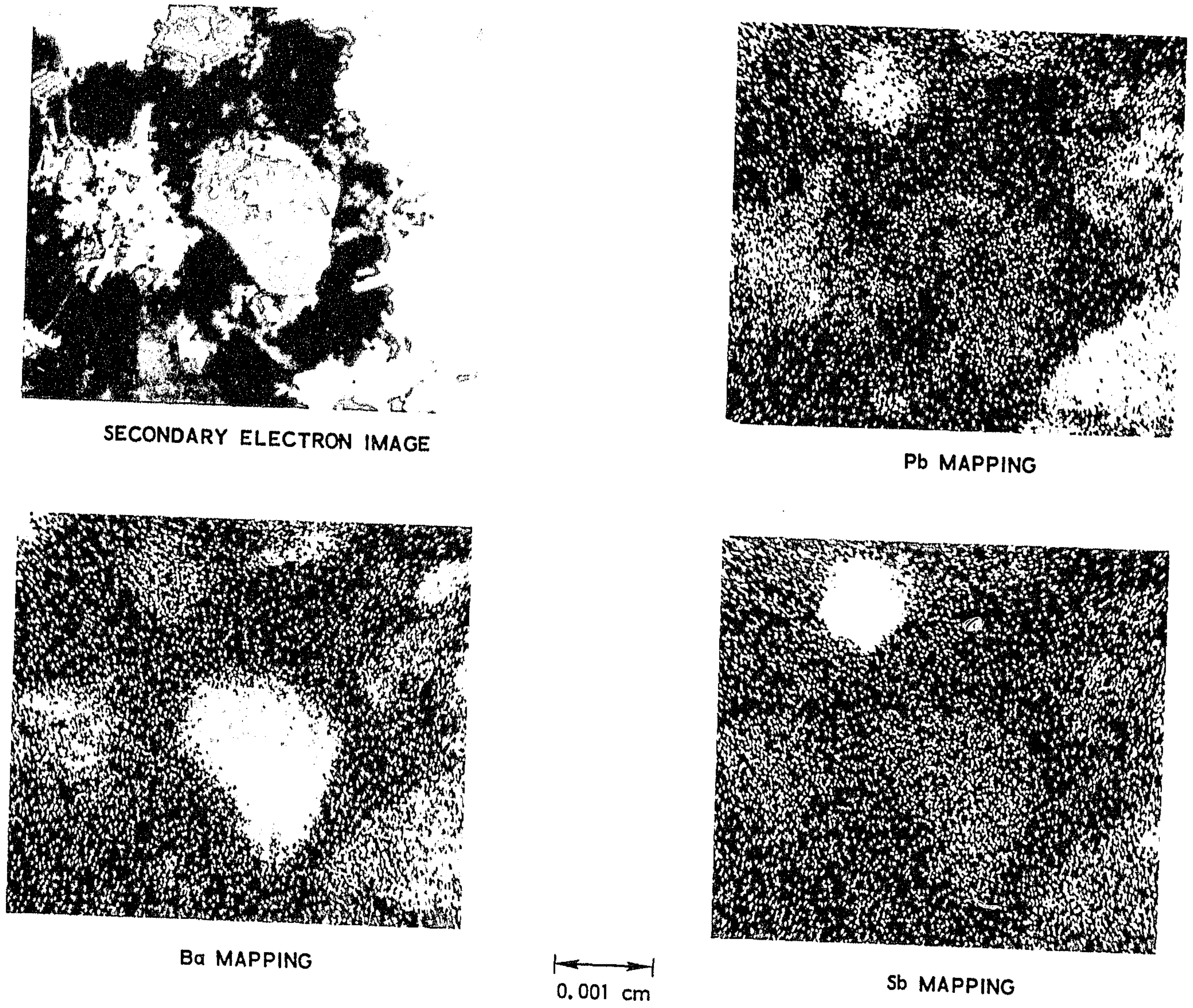
Basically, the current consensus on residue composition is that it contains organic and inorganic components. The organic components are primarily nitrocellulose and nitroglycerine decomposition products, as well as unburned material, and the inorganic materials derive largely from the primer and also from the bullet. Most primer compositions include substantial

amounts of lead styphnate (although there will be a tendency to reduce lead content because of toxicity as suitable substitutes are found) and many contain barium nitrate and antimony sulfide. Typical primer formulations are given in Table 1. Bullets normally contain lead alloyed with a few percent antimony and often a copper jacket, whereas the cartridge casing is normally of brass, which contains copper and zinc. Iron can be anticipated in residue as a result of gun barrel fragmentation. The metallic elements should be present in both elemental and compound form as solid particles. The identified organic decomposition products are gaseous under ordinary circumstances; therefore, they are not anticipated in particulate residues, although unburned propellant is almost certainly a component of particulate residue.

CHAPTER III. EXPERIMENTAL

The analyses were carried out with a JSM U-3 SEM equipped with a Nuclear Diodes lithium-doped silicon X-ray analyzer crystal of 160 eV resolution and an EDAX International, Inc., data processing system. The specimens reported here were coated with a conducting layer of carbon by an evaporation process that was controlled to give a layer of about 10^{-6} cm thickness. The coating operation requires 15 min and can be accomplished for several specimens simultaneously. The particle micrographs were obtained by using secondary electron imaging, and the X-ray analyses were obtained at 25 kV by using a beam current of about 10^{-10} ampere. Elemental analyses are reported in terms of X-ray counts per second for the strongest lines. Typical raw experimental data from the SEM are shown in Figures 1 and 2. In Figure 1, the secondary electron image of unfired primer is compared with X-ray elemental mappings of the same area for lead, antimony, and barium. The large central particle contains primarily barium, and the particle at top center contains largely antimony. Typical X-ray elemental analysis spectra for a single gunshot residue particle are shown in Figure 3a. Lead, antimony, and barium are identified in this particle. A spectrum that covers all elements of interest can be produced in less than 1 min with this method, whereas 15 min or more are required to map the spatial distribution of three elements (as in Figure 1).

The SEM has been proven to be very convenient because of the flexibility of the secondary electron imaging mode of detection. The focused electron

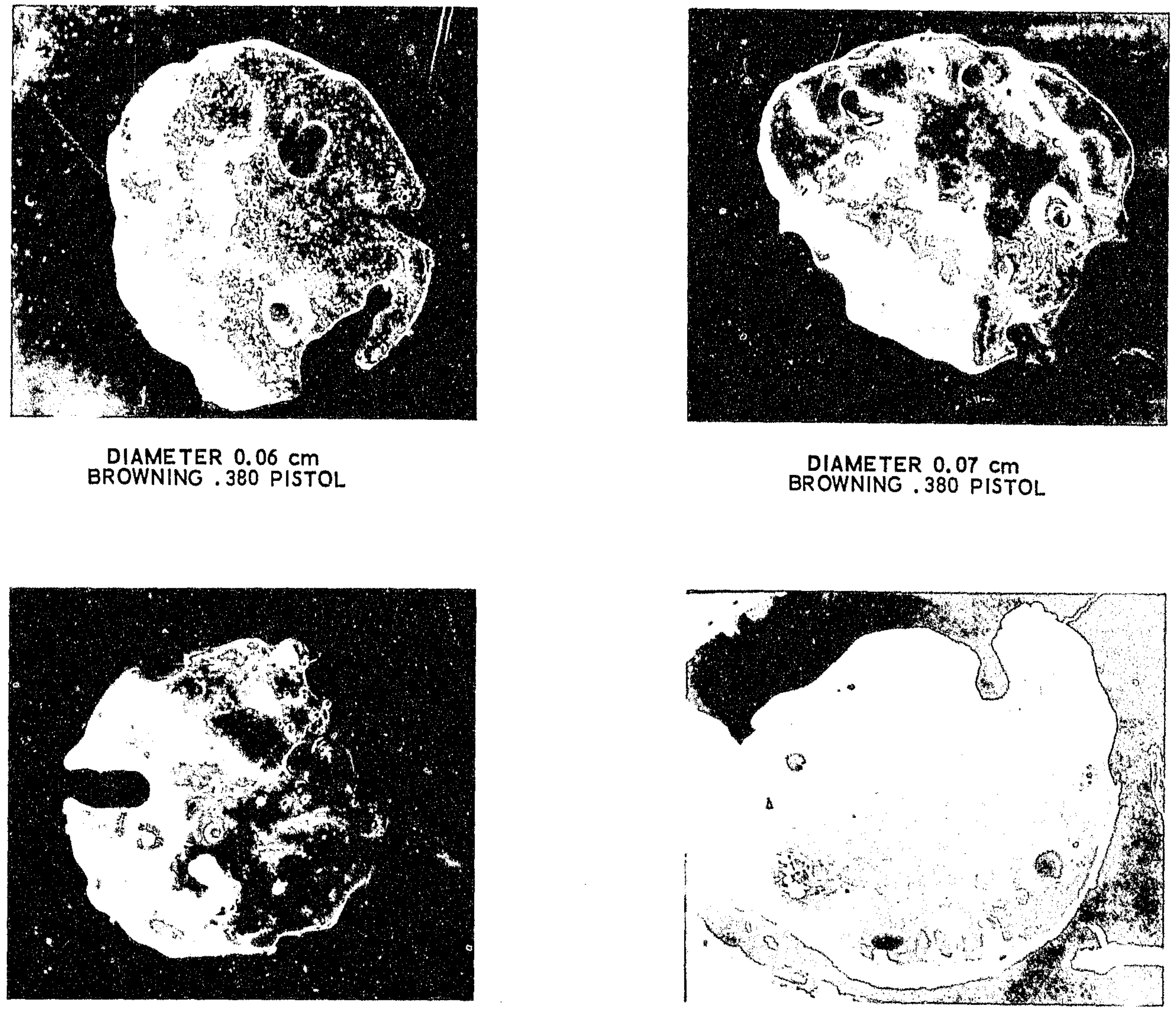

SECONDARY ELECTRON IMAGE

Pb MAPPING

Ba MAPPING

Sb MAPPING

Figure 1. Secondary Electron Micrograph and Elemental Mappings of Unfired Primer Obtained by SEM

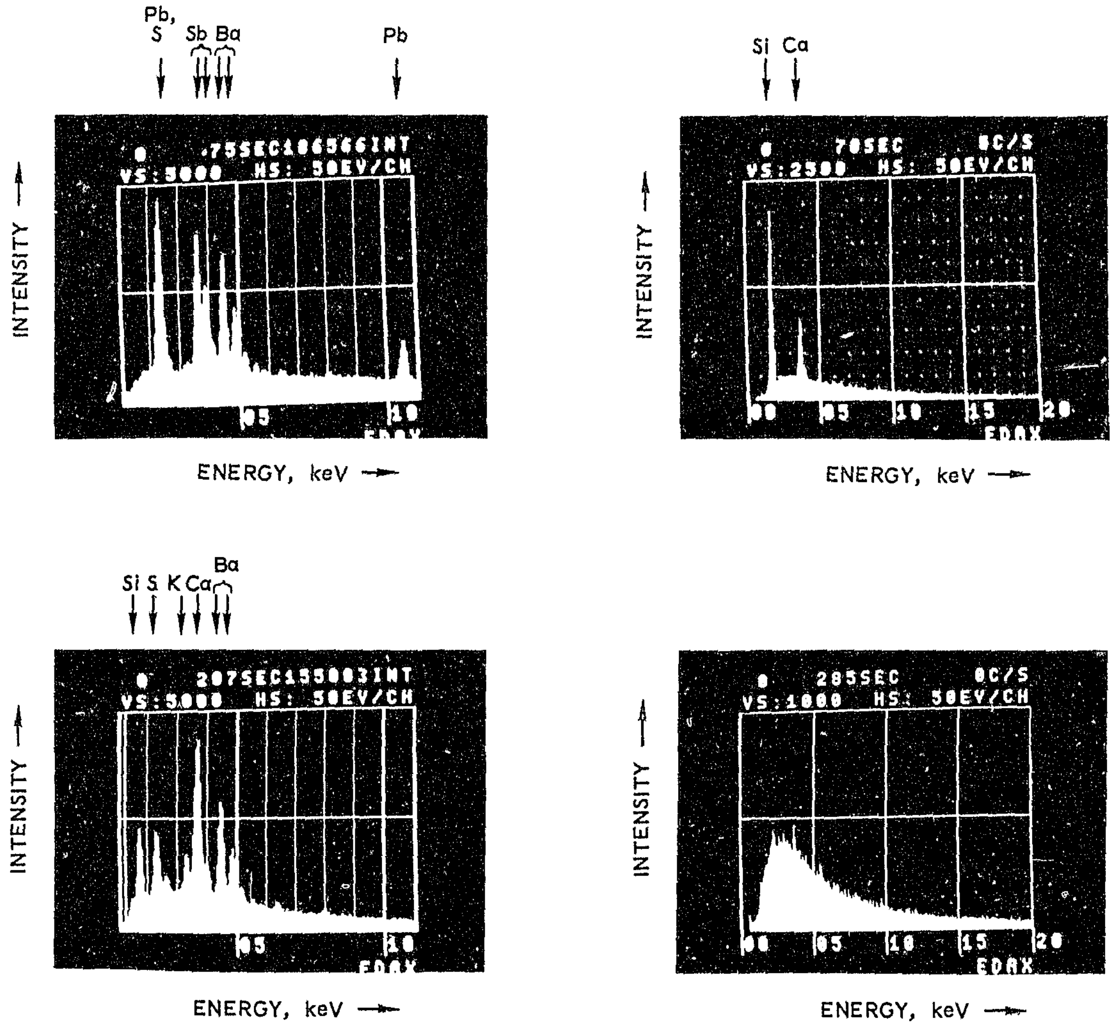

DIAMETER 0.06 cm
BROWNING .380 PISTOL

DIAMETER 0.07 cm
BROWNING .380 PISTOL

DIAMETER 0.06 cm
BROWNING .380 PISTOL

DIAMETER 0.07 cm
COLT .22 REVOLVER

Figure 2. Secondary Electron Micrographs of Typical Partially Burned Smokeless Powder Particles by SEM



a.

ANALYSIS OF
THE SPHERICAL
GUNSHOT RESIDUE
HANDSAMPLE
PARTICLE SHOWN
IN FIGURE 6a

b.

ANALYSIS OF
THE TYPICAL
ENVIRONMENTAL
HANDSAMPLE
PARTICLE SHOWN
IN FIGURE 9b

c.

ANALYSIS OF
NONDESCRIPT
GUNSHOT RESIDUE
PARTICLE FROM
HANDSAMPLE.
CALCIUM AND
SULFUR ARE
PROMINENT,
AND LEAD IS
NOT OBSERVED
IN THIS ATYPICAL
PARTICLE.

d.

ANALYSIS OF
EPITHELIAL
PARTICLE FROM
HANDBLANK
THE X-RAY
EMISSION
IS DUE TO
BREMSSTRAHLUNG
RATHER THAN
DISCRETE
ELEMENTAL LINES.

Figure 3. Energy-Dispersive X-ray Spectra of Particles by SEM

beam strikes the target specimen surface and transfers its high energy to the electrons of the sample. Secondary electrons are then ejected from the specimen surface because of the excess energy. This excitation only spreads over a volume with a diameter of 10^{-6} cm; thus, the 10^{-6} cm focal diameter of the scanning beam is not appreciably degraded. The efficiency of secondary electron production is influenced by such factors as the elemental composition of the outermost 10^{-6} cm of the specimen surface (heavy elements are the more efficient emitters), the geometry of the emitting surface with respect to the detector, and the electrical conductivity of the surface. In order to form a micrograph, the electron beam is scanned across the specimen surface in a raster, and the intensity of the emitted secondary electrons is displayed on a cathode ray tube (CRT) as a function of beam position. If the specimen is a nonconductor, the beam charges the surface, which results in a loss of beam focus because of coulombic repulsion; if there are particles on the surface that are not rigidly attached, they will be dislodged due to coulombic repulsion. This problem is overcome by coating nonconductive specimens with conductive material. Carbon has been most satisfactory in this work because it has a low secondary electron background and does not produce interfering X-ray lines. The coating is achieved by vacuum subliming carbon onto the specimen surface for a period of time sufficient to produce a layer about 2×10^{-6} cm thick. There is some local heating at the point of beam impact. It is severe if the beam current is high and the thermal conductivity of the specimen is low. Therefore, low currents were normally used in order to avoid decomposition of organic compounds and dislodgement of small particles.

Elemental analyses are obtained with a SEM by analyzing the X rays that are generated as the electrons of the atoms that have been excited by beam impact return to lower levels of excitation. The energies of useful X-ray fluorescence lines are shown in Table 2. This process is much less efficient than secondary electron production; therefore, the X-ray signals must be averaged over much longer periods of time. The X-rays are generated over a much larger volume than are the secondary electrons. A tear-drop-shaped region with a depth of about 10^{-4} cm (dependent on the elemental composition) is excited; therefore, X-ray analysis is more representative of the region under the surface than the surface itself.[27] Efficient detection is achieved with a semiconductor crystal detector such as lithium-drifted silicon. The silicon crystal becomes more conductive when it absorbs an X-ray photon emitted by the specimen, and the amount of conductivity increase is dependent on the X-ray energy. These detectors have a maximum resolution of about 160 eV, which is sufficient for identification of most elements. The efficiency of X-ray detection is highly dependent on atomic number, and aluminum is the lightest element that has been detected in this work. The atomic number of aluminum is 13. Magnesium (12) is detectible in Mg-bearing minerals, but sodium (11) is not usually detected. Elemental analyses by SEM with X-ray detection is qualitative or, at best, semiquantitative unless elaborate data-processing techniques are used. The problems of quantitation by SEM X-ray analysis have been discussed in the literature.[27]

The energy resolution of X-ray detection can be improved by orders of magnitude by using a specialized instrument equipped with crystal spectrometers, which provide wavelength dispersive detection. Traditionally,

Table 2. Energies of Principal X-ray Emission Lines for Elements Found in Gunshot Residue Analyses[a]

Element	Emission Lines (energy in keV)[b]					
	K_α	K_β	L_α	$L_{\beta 1}$	$L_{\beta 2}$	L_α	M
Si	1.739						
S	2.307	2.465 (10%)					
Cl	2.621	2.815 (8%)					
K	3.312	3.589 (15%)					
Ca	3.690	4.012 (15%)					
Ti	4.508	4.931 (20%)					
Fe	6.398	7.057 (20%)					
Ni	7.471	8.263 (20%)					
Cu	8.040	8.804 (20%)					
Zn	8.630	9.570 (20%)					
Br	11.907	13.286 (24%)					
Sb			3.604	3.843 (75%)	4.100 (17%)		
Ba			4.465	4.829 (50%)	5.193 (20%)		
Pb			10.550	12.612 (50%)	12.621 (20%)	14.762 (10%)	2.380

[a] Intensities of lines relative to the parent line are in parentheses.

[b] 1 keV = 1.6021×10^{-16} joule = 3.83×10^{-17} g cal.

instruments with this capability have been called electron microprobe analyzers; they separate X-ray emissions from all observable elements, but at a cost in sensitivity. The X-ray analysis of a single point on a specimen by this technique requires significantly more time than is required by energy dispersive X-ray analysis. Normally, the specimen is viewed through an optical microscope rather than by secondary electron imaging in this technique because the beam cannot be rastered significantly in two dimensions during X-ray analysis, inasmuch as the beam impact point defines the slit of the crystal spectrometer. Instruments have been built that combine features of the two types discussed, but they are not widely available.

The ion microprobe mass analyzer has also been useful for research on the detection of residue particles, but it is clearly not suited for routine residue detection applications, partly due to the expense involved. It creates a focused beam of either oxygen, nitrogen, or argon ions that strike the specimen and sputter off (eject) ions created from the surface atoms. These ions are then mass analyzed in a mass spectrometer for identification of atomic and molecular ion fragments. This is the most sensitive analytical instrument — it has an ultimate detection limit of 10^{-19} g for some elements and can detect all other elements with slightly lesser efficiency. It analyzes material in the first few atomic or molecular layers. However, the surface is eroded by the sputtering; therefore, it is possible to bore through the specimen surface and obtain three-dimensional analysis of composition. The method has been valuable in establishing the organic nature of some residue particles and the presence of thin heavy metal surface layers on these particles.

Test firings were conducted at indoor and outdoor ranges with several guns:

- .22 caliber Colt revolver
- .22 caliber Ruger revolver
- .380 caliber Browning semiautomatic pistol
- 9 mm caliber Browning high-power semiautomatic pistol
- .38 Special Smith and Wesson revolver
- .45 caliber 1911 Colt semiautomatic pistol

The pure residue specimens, including muzzle discharge particles, were collected in polyethylene bags that surrounded the gun during firing. Particles were than removed from the inside surfaces of the bags. The pure residue that reaches the hand was collected by covering the firing hand with a latex glove, or by covering the surface of the hand with an adhesive layer prior to firing. Unless otherwise stated, handsamples, as distinguished from pure residue, were collected from the hand immediately after firing on adhesive layers (Scotch 465 adhesive) attached to 2.5-cm-diam aluminum disks that also served as SEM sample supports. In tests of identification capability, efforts were made to provide dirty and clean handblanks and to have ordinary amounts and types of contaminants on the hand prior to firing in order to simulate natural circumstances. Of the guns used, the Browning .380 semiautomatic and Colt .22 revolver had considerable wear, and the Browning .380 provided copious quantities of large black particles that were easily visible on the hand. The .38 Special revolver, the 9 mm semiautomatic, and the .22 caliber single-action Ruger revolver were essentially new guns that ejected no visible residue particle onto the firing hand. In firing tests, care was taken to avoid contamination of the firing hand by loading operations.

CHAPTER IV. RESULTS

In this study, electron microscopy was used to improve the ability to characterize gunshot residue and thus identify residue in the presence of hand contaminants. The guns studied produced substantial residue deposits when the muzzle discharge was included in the residue. Visually, the most prominent part of these deposits was black specks, as large as 0.1 cm, that resembled smokeless powder when examined under a low-power optical microscope (Figure 4). Their shapes were irregular, as if the particles were the fragmented and partially burned remnants of smokeless powder. Residue deposited on the hand by the Browning .380 semiautomatic, the .32 Llama semiautomatic, and, to a lesser extent, the Colt .22 revolver contained these black specks. They were infrequently observed in residue from the Smith and Wesson .38 Special and the single-action .22 caliber Ruger revolvers. The cartridge ejection mechanism of the Browning .380 discharged these particles, and the worn gap between the cylinder and barrel in the Colt .22 permitted escape of this residue toward the firing hand.

These large particles were the most striking feature of the pure residue in the SEM photomicrographs. They ranged from 10^{-3} to 10^{-1} cm; typical examples are shown in Figure 2. At low SEM magnification (100 X), smoothly contoured surfaces and edges with craters of round cross sections penetrating into or through the surfaces were observed. At higher magnification, which was required for examination of the smaller particles, the

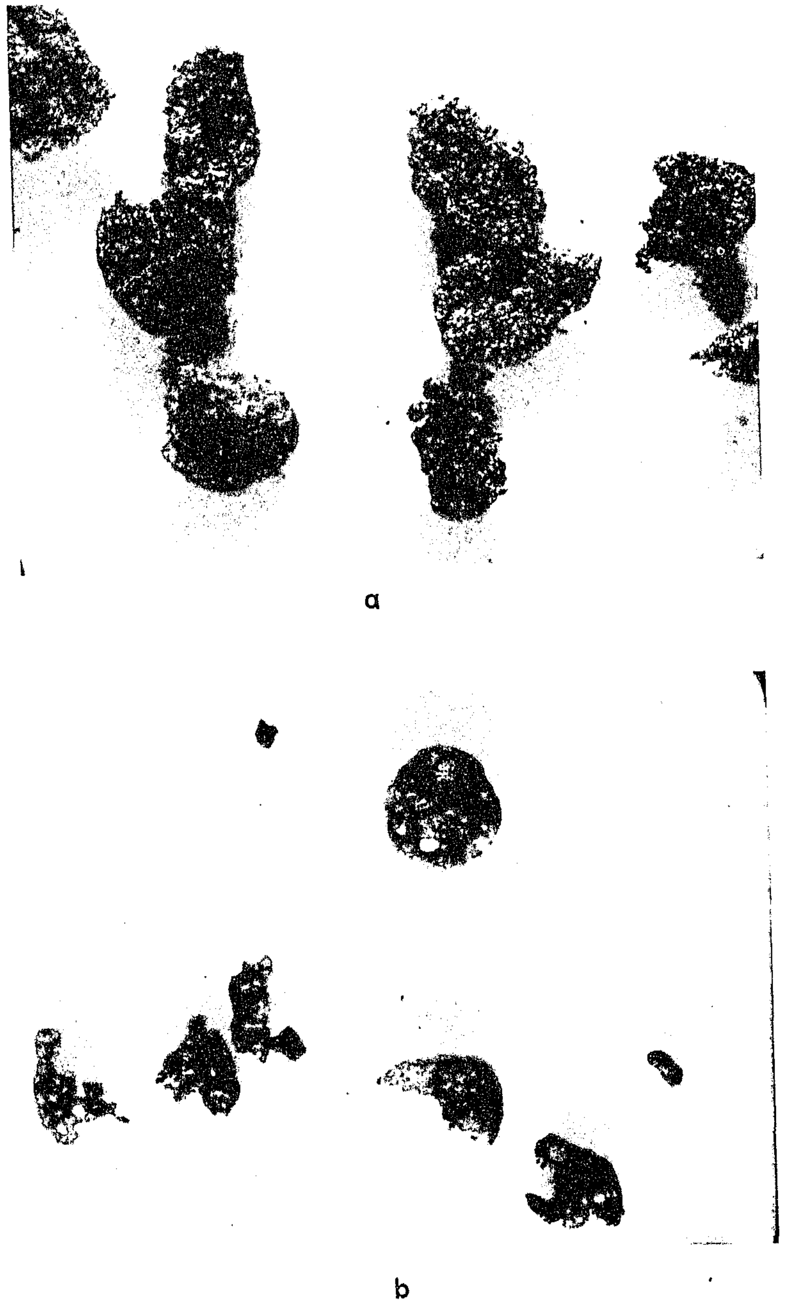
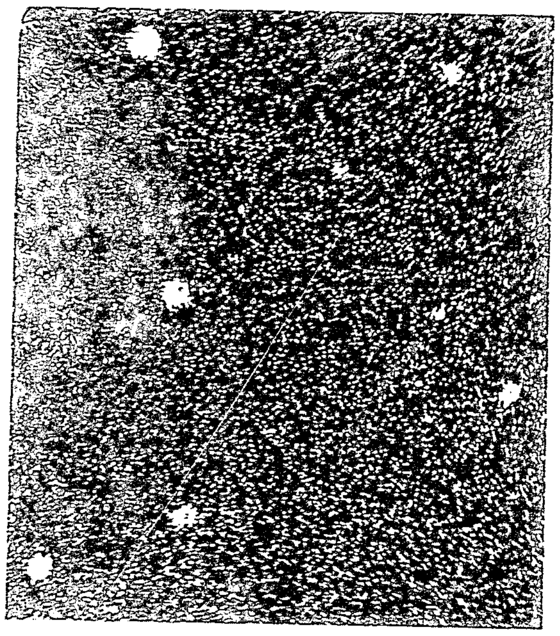


Figure 4. Macrophotographs of Smokeless Gunpowder. a. Smokeless gunpowder grains from an unfired .380 caliber Remington cartridge; the particles have a maximum dimension of 0.1 cm; b. Partially burned gunpowder from a Remington cartridge from a .380 caliber Browning semiautomatic pistol.

surface was rough, often with a sponge-like or cratered appearance. The X-ray signals of lead, antimony, and barium averaged over the surface of these particles by scanning electron microscopy were consistent with a low concentration of these elements. A barium mapping of one of these characteristic particles by scanning electron microscopy is shown in Figure 5. There is striking evidence that the barium is concentrated in the round spots on the particle surface. X-ray analyses confined to regions of the large particles that did not have the round particles present indicated absence of heavy metals. The comparative abundance of Bremsstrahlung radiation in the latter regions can be interpreted as arising from light elements such as those contained in organic materials. Typical properties of a large number of these particles are summarized in Table 3.

The highly sensitive technique of ion microprobe mass analysis (IMMA) was used to provide further analysis of these large particles because it responds to organic compounds. Because the technique is about 10^6 times more sensitive than SEM X-ray analysis, lead, antimony, and barium could be detected in the surface of the large particles, even for regions that did not have spherical particles. However, during the process of analysis, as the ion beam bored into the particle surfaces, the signal from these elements vanished, which indicated that a thin layer containing these elements had been present on the surface. The surface areas of the large particles that were not covered by round spots were composed of compounds that fragmented into

SECONDARY ELECTRON IMAGING. SPHERES HAVE DIAMETERS ABOUT 5×10^{-4} cm.



BARIUM MAPPING USING X-RAY MAPPING OF SAME AREA SHOWN BY SECONDARY ELECTRON IMAGING

Figure 5. Surface of a Partially Burned Smokeless Powder Particle by SEM at High Magnification

Table 3. Characteristics of Particles Analyzed from Various Residue Specimens by SEM

Colt .22 Revolver; Western,[a] Remington,[b] and Federal[c] Ammunition (41 particles examined)						
	Partially Burned Smokeless Powder Fragments, Pure Residue (5 examined)[g]		Spherical Particles Handsample (10 examined)		Nondescript Particles Handsample (26 examined)	
	Median	Range	Median	Range	Median	Range
Diameter	0.05 cm	0.003-0.07 cm	0.0007 cm	0.0003-0.004 cm	0.0015 cm	0.0005-0.01 cm
Number embedded spheres	60	16-60				
Lead[d,f]	250	100-350	400	40-1400	250	0-1900
Barium[f]	0	0-20	150		30	0-500
Antimony[e,f]	0	0-30	0	0-43	0	0-140
Additional elements	0	0	0	0-2	1	1-4
Browning .380 Semiautomatic Pistol; Remington[h] Ammunition (30 particles examined)						
	Partially Burned Smokeless Powder Fragments, Handsample (8 examined)[i]		Spherical Particles Handsample (10 examined)		Nondescript Particles Handsample (12 examined)	
	Median	Range	Median	Range	Median	Range
Diameter	0.05 cm	0.01-0.07 cm	0.001 cm	0.0006-0.006 cm	0.02 cm	0.001-0.02 cm
Number of spheres	50	3-160				
Lead[d,f]	50	0-200	300	0-500	90	30-400
Barium[f]	80	0-600	180	0-700	60	0-700
Antimony[e,f]	0	0-400	40	0-500	0	0-80
Additional elements	3	0-6	0	0	0	0
Smith and Wesson .38 Special Revolver; Western[h] and Remington[h] Ammunition (45 particles examined)						
	Partially Burned Smokeless Powder Fragments, Handsample (2 examined)[i]		Spherical Particles Handsample (21 examined)		Nondescript Particles Handsample (22 examined)	
	No. 1	No. 2	Median	Range	Median	Range
Diameter	0.05 cm	0.05 cm	0.003 cm	0.0007-0.005 cm	0.003 cm	0.0005-0.05 cm
Number of spheres	4	10				
Lead[d,f]	200	70	300	0-2200	200	0-1100
Barium[f]	22	0	100	0-1200	20	0-800
Antimony[e,f]	0	0	0	0-100	0	0-10
Additional elements	1	3	2	0-5	3	0-7

[a] Of particles examined from this ammunition, 28% contained two or more of the elements lead, antimony, and barium; the pure primer contained lead and barium but no antimony.

[b] Of particles examined from this ammunition, 8% contained two or more of the elements lead, antimony, and barium; the pure primer contained only lead.

[c] Of particles examined from this ammunition, 59% contained two or more of the elements lead, antimony, and barium; the pure primer contained lead, barium, and antimony.

[d] Based on lead M line, which is frequently overlapped by the sulfur K lines.

[e] Based on the antimony L lines, which are frequently overlapped by the calcium K_α line.

[f] The measurements are in terms of counts/sec at the peak intensity, using 50 eV per channel.

[g] It is possible that the smaller particles in the size range of 0.003 to 0.01 cm are inorganic and have sperical inclusions on the surface.

[h] The pure primer contained lead, barium, and antimony.

[i] Elemental analysis was not necessarily averaged over the entire particle surface.

light elements and molecular ion fragments that were consistent with a smokeless powder precursor. Therefore, it is likely that the large particles are fragmented grains of partially burned smokeless powder (single base is nitrocellulose, and double base is nitrocellulose plus nitroglycerine). Identification of specific molecular components in residue by IMMA mass spectra is not easily accomplished because different molecular ion fragments can have the same mass, and these masses can be the same as those of ionized atoms. For lead, barium, and antimony atomic ions, the natural isotopic abundance readily distinguishes them from molecular ions.

The large particles can be rapidly located and identified by visual inspection by using the SEM with secondary electron imaging. The particles either structurally decomposed or dislodged rapidly when examined with high-electron-beam currents. (High currents were associated with the continuous display CRT mode of the SEM and with normal analysis by electron microprobe and IMMA.) This is consistent with the low thermal stability of smokeless powder. The particles with high concentration of heavy metals were stable at high beam current (provided they were rigidly attached to the instrument specimen support) because of the higher thermal conductivity and great thermal stability of the materials.*

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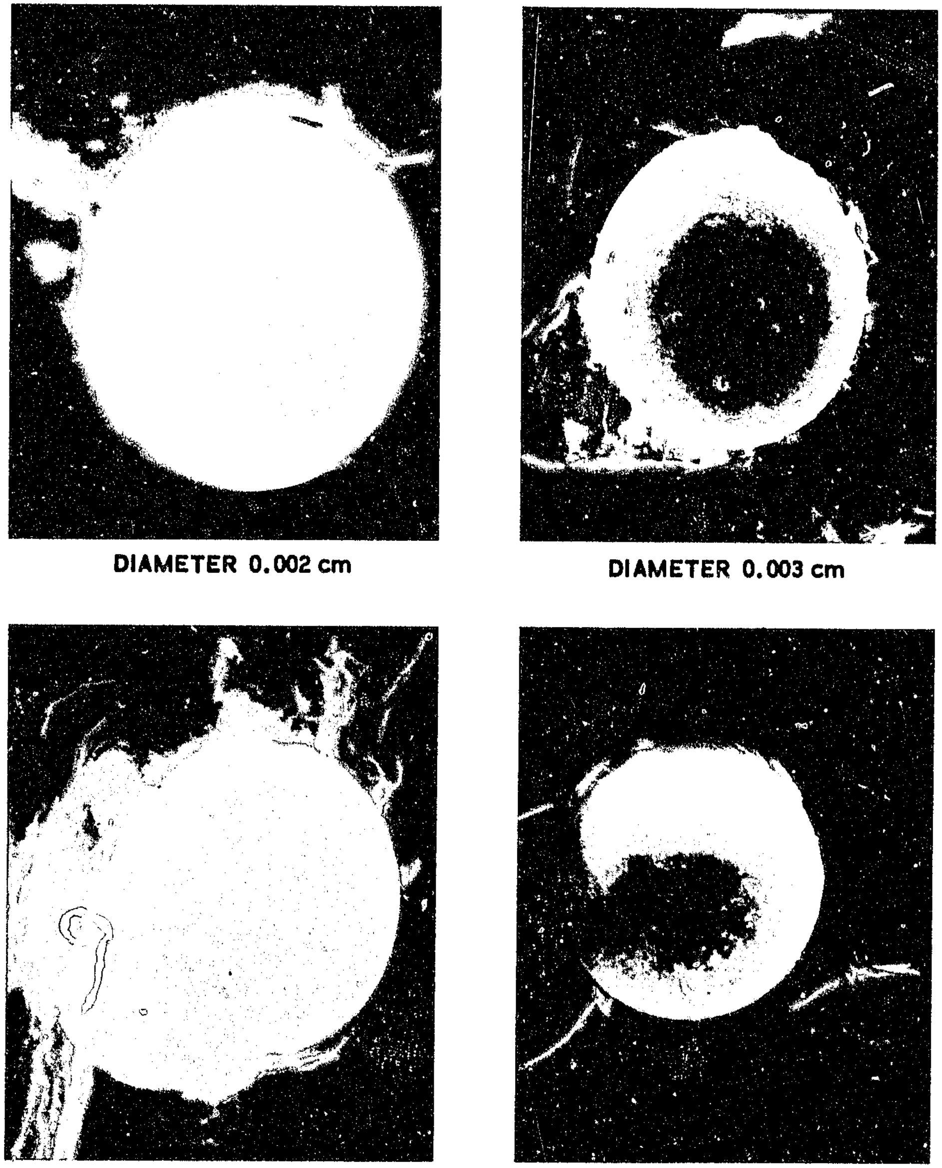
*The beam-induced structural decomposition of smokeless powder may be useful for residue characterization because the particle surface cracks in the process of heating during observation, and then material from the interior of the particle appears to flow into the vacuum. (Some other organic materials have been observed to behave in this manner.)

The round spots on the surface of the large organic particles were studied in detail because of their potential value as identifying features of residue. These spots were spherical or spheroidal at high magnification with secondary electron imaging (Figure 6). X-ray analysis confined to individual spheres invariably revealed lead, antimony, or barium signals that were consistent with the particles being largely composed of these elements. Lead is most frequently encountered, even for ammunitions that have primers rich in antimony and barium. Silicon, calcium, sulfur, ion, and copper are also often associated with these residue particles, but not regularly or in any fixed ratios. Often, calcium interfered with antimony measurement. Typical analysis results for this class of particles are summarized in Table 3, and the X-ray spectrum from a typical spherical particle (Figure 6a) is shown in Figure 3a.

The spherical features ranged from 3×10^{-3} to 3×10^{-4} cm and were invariably found on the surface of the large particles, but also occurred in abundance as separate isolated particles of the residue. These comprised the only regions with high concentrations of heavy metals on the surface of the partially burned smokeless powder particles.

Particles of nondescript morphology that ranged from 5×10^{-4} to 5×10^{-2} cm were abundant in residue handsamples and pure residue. Several of these particles are shown in Figure 7. Some appear to be metal fragments, others appear to be clumps of composite materials that might be produced subsequent to the combustion process. No common features that could



a.

BROWNING .380
PISTOL

Pb 500 COUNTS/sec
Sb 400
Ba 300

DIAMETER 0.002 cm

b.

SMITH AND WESSON
.38 SPECIAL REVOLVER

Pb 60 COUNTS/sec
Sb 0
Ba 900

DIAMETER 0.003 cm

c.

COLT .22
REVOLVER

Pb 600 COUNTS/sec
Sb 0
Ba 0

DIAMETER 0.0007 cm

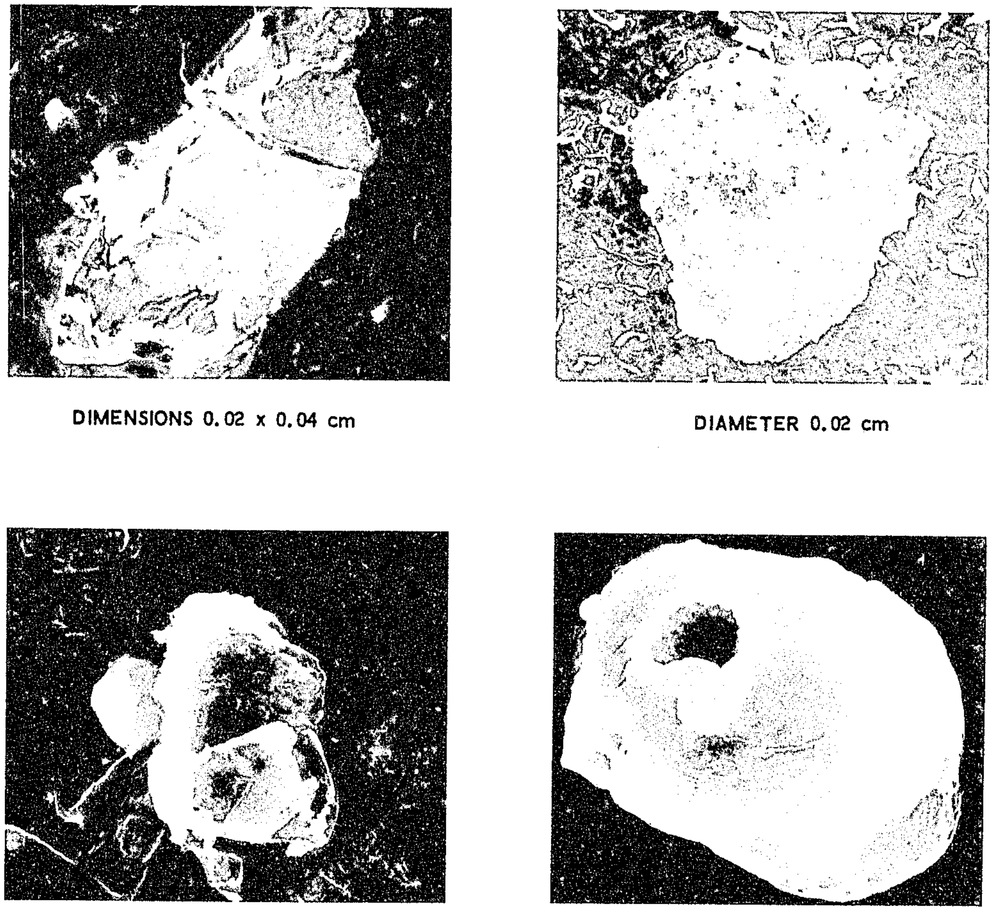
d.

COLT .22
REVOLVER

Pb 96 COUNTS/sec
Sb 0
Ba 29

DIAMETER 0.001 cm

Figure 6. Typical Spherical Particles from Handsamples Obtained by Secondary Electron Imaging



BROWING .380 PISTOL

Pb 50 COUNTS/sec
Sb 80
Ba 140

DIMENSIONS 0.02 x 0.04 cm

SMITH AND WESSON .38
SPECIAL REVOLVER

Pb 120 COUNTS/sec
Sb 0
Ba 90
Fe 230
Cu 130
Al 90
Ca 70

DIAMETER 0.02 cm

SMITH AND WESSON .38
SPECIAL REVOLVER

Pb 0 COUNTS/sec
Sb 0
Ba 100
Ca 150
Si 80
S 70
K 40

DIAMETER 0.003 cm

COLT .22
REVOLVER

Pb 50 COUNTS/sec
Sb 50
Ba 110
Cu 6

DIMENSIONS 0.002 x 0.003 cm

Figure 7. Secondary Electron Micrographs and X-ray Fluorescence of Typical Nondescript Gunshot Residue Particles

be used to distinguish between residues produced by various guns and ammunition were recognized for the nondescript particles, but analysis efforts were cursory. For the guns studied, these particles and the spherical particles comprise the largest fraction of the residue that deposits on the hand. Lead was commonly the element of highest concentration. Although antimony is present in many primer compositions (all but some .22 caliber ammunition), it was frequently observed to be of low concentration in residue particles. This could be additional evidence in support of Bashinski's findings that nonjacketed bullets are major sources of lead and antimony in residue because bullet lead is normally alloyed with about 5% antimony in order to achieve the desired degree of hardness. Since the most common primer formulations contain about 30% antimony, as shown in Table 1, the addition of bullet material to the vaporized primer residue would reduce the concentration of antimony in most residues. The related observation that antimony was present in some particles produced by ammunition with antimony-free primers also supports Bashinski's conclusions[21] and is consistent with neutron activation analysis work, which has also shown that antimony can be detected in residue from ammunition with antimony-free primers.[15]

As in past studies, a wide variation in particle composition was observed in terms of ratio of concentrations of lead to antimony to barium for particles from a single discharge. Additionally, other elements were often present at high concentrations. In order of decreasing frequency of appearance, these were: calcium, silicon, iron, copper, sulfur, potassium,

and aluminum. The energies of X-ray lines that were used for analysis are given in Table 2. The principal X-ray line of calcium is the K_α at 3.7 keV, which overlaps the antimony L doublet when energy dispersive detection is used. Therefore, the analyst must be alerted to the necessity to judge the presence of antimony on the basis of the occurrence of the partially resolved L doublet at 3.6 keV, with the intensity ratio 1:0.8. The antimony doublet is shown in Figure 3a; the calcium line is shown in Figure 3b.

Sulfur is detected by its K lines at 2.307 and 2.465 keV, which are not resolved and also overlap the lead M line at 2.38 keV. These lead and sulfur lines are shown in Figures 3a and 3c, respectively. Therefore, the lead L_α line at 10.5 keV must be used in order to confirm the presence of lead. For excitation with 25 kV electrons, the ratio of lead L_α to M intensity is about 0.3; therefore, it is advantageous to judge the concentration of lead from the L_α line, which is not overlapped at 160 eV resolution.*

Wavelength dispersive detection was also applied to gunshot residue particle analysis by means of an electron microprobe. The technique easily resolved lead from sulfur and antimony from calcium; the results indicated that these elements often occur together in particles. (This is expected because many primers contain sulfur in the form of antimony sulfide and

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*The ratio of lead L to M intensity varied considerably from specimen to specimen under identical SEM conditions. This can be explained by the influence of different local matrices.

calcium in the form of calcium silicide, as shown in Table 1.) Shown in Figure 8 are elemental analysis spectra obtained by using the electron microprobe with the two crystals that are required to cover the same range that energy dispersive analysis covers with a single detector crystal.

A. Handblanks

Representative handblanks were examined by SEM during the course of work in order to establish a basis for differentiation of handblank particles from gunshot residue. Secondary electron micrographs and X-ray analyses of representative particles are shown in Figure 9. The most frequently detected elements were silicon, iron, calcium, sulfur, chlorine, potassium, titanium, zinc, copper, and aluminum. If a particle reveals only these elements during SEM examination, it is highly likely that the particle is from an environmental source. Organic particles from the hand are abundant in handlifts; fortunately, their morphology is easily recognized, and their X-ray fluorescence is weak, mainly because of Bremsstrahlung of light elements. In an average handblank, there are also a large number of mineral particles that contain silicon, calcium, or titanium. They have smooth surfaces with a crystalline appearance. Fibers are common — they contain primarily light elements and occasionally sulfur or chlorine. Particles from more than 20 handblanks were examined and none would be confused with gunshot residue. Automobile exhaust from leaded gasoline produces the particles that most resemble gunshot residue, particularly with respect to lead content and size. However, bromine has always been a prominent constituent of these

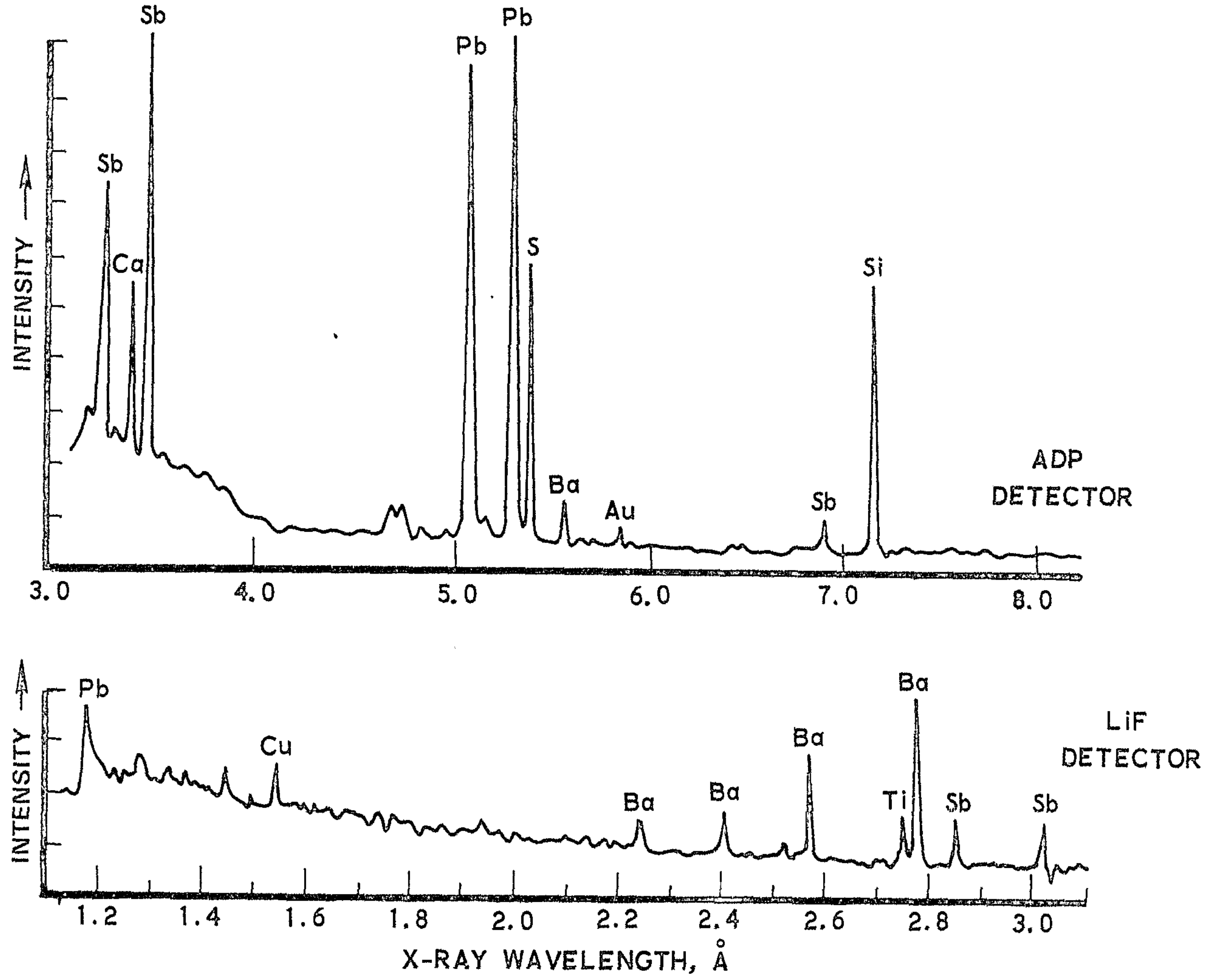
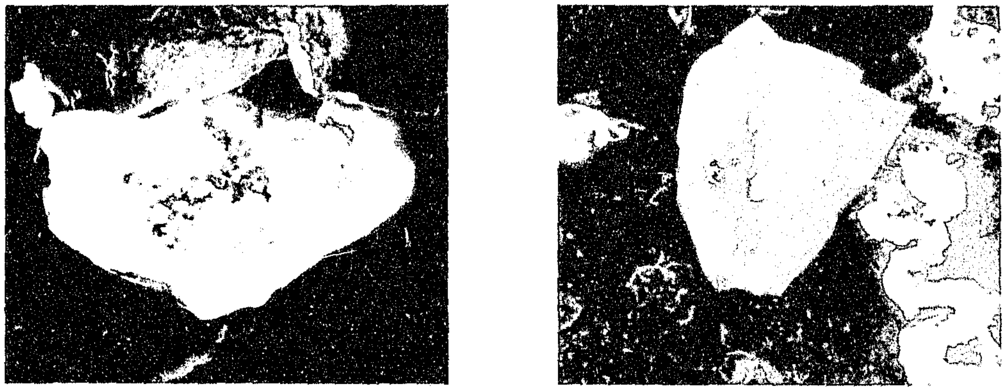


Figure 8. Electron Microprobe Analysis of Gunshot Residue Primer Specimen Coated with a Gold Conductive Layer



a.

AUTOMOBILE
EXHAUST
PARTICLE

Pb 300 COUNTS/sec
Br 50
Ni 30

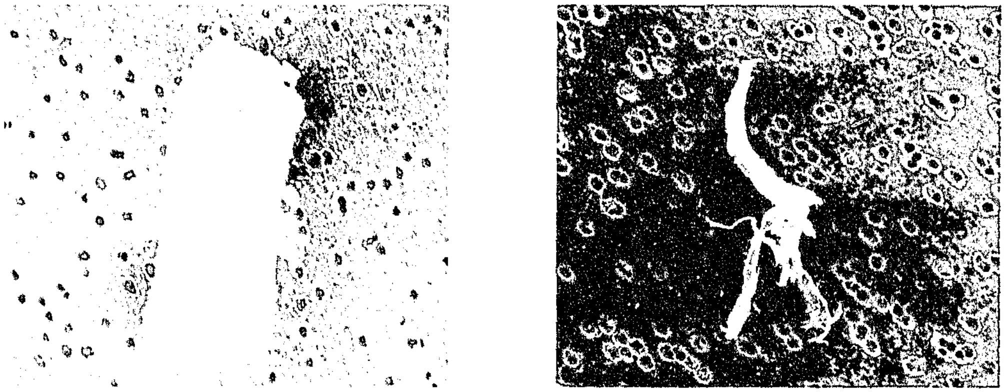
DIMENSIONS 0.002 x 0.003 cm

b.

MINERAL MATERIAL
WITH SMOOTH
SURFACES AND
EPITHELIAL
MATERIAL

Si 290 COUNTS/sec
Ca 86

DIMENSIONS, MINERAL PARTICLE,
0.01 x 0.015 cm



c.

MINERAL
PARTICLE

Si 500 COUNTS/sec

DIMENSIONS 0.005 x 0.015 cm

d.

EPITHELIAL MATERIAL

300 COUNTS/sec

INTEGRATED OVER
ALL ENERGIES

DIMENSIONS 0.001 x 0.01 cm

Figure 9. Secondary Electron Micrographs and X-ray Fluorescence Analysis of Typical Handblank Particles

contaminant particles, as shown in Figure 9a, whereas it is not detected in gunshot residue particles. The X-ray analysis spectrum of the mineral particle shown in Figure 9b is shown in Figure 3b, and the epithelial particle shown in Figure 9d produced the Bremsstrahlung of Figure 3d.

B. Handsamples and Identification Test

Once the SEM microscopist becomes familiar with the appearance of gunshot residue particles, it is possible to rapidly select likely residue particles from the diverse particles present in the average handsample. When a candidate particle is selected on the basis of appearance as the specimen block is being scanned, a rapid examination of the X-ray spectrum of the particle for lead is useful in evaluating the nature of the particle. It is often most advantageous to scan the specimen rapidly at low magnification in a search for large, partially burned smokeless powder particles, then make a search for spherical particles and do X-ray analysis on them. If none are found, a careful search is made for the less distinctive nondescript particles.

In order to test the success in identification of gunshot residue specimens from a mixed group of residue specimens and handblanks, a blind test was carried out. Handsamples were obtained on an adhesive layer attached to 2.5-cm-diam aluminum blocks. These specimens were carbon coated and then analyzed by SEM. Of 31 specimens, 15 were firing specimens and 16 were handblanks. All were identified correctly by the microscopist, who was not aware of specimen identity. Less than 1 hr was required for analysis of each specimen. The firing handsamples were produced by single firings of .22, .38, .380, .45, and 9 mm caliber guns. Both revolvers and semiautomatics were used in order to obtain representative results. With the higher caliber semiautomatic and worn revolvers, particulate deposit was rich, and positive analyses required only brief searches for suitable particles. For sparse residue specimens such as those produced by clean guns, e.g., the new single-action .22 Ruger revolver, it was difficult to locate particles of interest, and a large number of environmental particles were subjected to X-ray analysis before a gunshot residue particle was identified.

CHAPTER V. DISCUSSION

A. The Nature of Residue

The three particle categories that have been proven useful for analysis of residue characteristics can provide the framework for identification of unknown specimens. The large particles of partially burned smokeless powder are most easily located and identified. The spheres are also quite characteristic of residue, but are more difficult to locate because the small size necessitates scanning over large areas of the specimen at high magnification. The nondescript particles are the most difficult to distinguish from contaminant particles, but they comprise a large part of the residue. Therefore, they may be of principal interest in identification of sparse handsamples taken an appreciable time after firing.

The large partially burned powder particles have highly distinctive morphologies and have been recognized previously in the work of Boehm,[11] who obtained electron micrographs of such particles on cloth. The particles can be seen by the naked eye and are responsible for the reaction that is used in the dermal nitrate test. They have been identified in a variety of past work, including an autoradiographic study of residue deposits, where they were observed as a particle class that could be differentiated from radioactive spots not associated with visible deposits and from the smoke deposit that causes spatially uniform autoradiographic exposure.[19] Autoradiography responds to the antimony and barium in these particles, and the sodium rhodizonate method has been used to prove that they contain lead. Therefore, the results of this investigation of the large particles, which confirm the simultaneous presence of an organic substrate together with surface deposits of the lead, antimony, and barium, are entirely consistent with prior work. The surface deposits consist, at least partially, of the spherical globules that are composed of lead, barium, or antimony.

The spherical globules are present on the surface of unburned powder particles and as separate entities. Since their size ranges from 10^{-4} to 3×10^{-3} cm, they would be considered to be a dust or smoke. Therefore, it can be anticipated that they are among particles of the smoke deposits detected by autoradiography and the sodium rhodizonate test. The micron-size particles are expected to remain suspended in air for an appreciable time; thus, they probably constitute a part of the airborne residue studied by Renfro and Jester.[8] Small molten droplets of metals or salts, for example, assume spherical configuration in a gaseous or liquid environment because the spherical form minimizes the surface energy of the particle. Therefore, it is reasonable to assume that the spherical particles in gunshot residue are formed by condensation of molten droplets of spent primer compounds and metals from the bullet and cartridge casing. The spherical shape should be retained upon solidification if the mixture has a composition that results in an amorphous or very fine-grained phase. If the composition results in a more coarsely crystalline phase, the nondescript particles that are so prevalent in the residue can be produced.

The results from SEM X-ray analysis and electron microprobe study of the small particles indicate that they are largely composed of lead, barium,

antimony, silicon, calcium, and sulfur. The chemical form of the materials remains unknown: such materials as metal oxides and sulfides may predominate,[24] or some particles could be metal solutions. This is expected to be the case if the bullet lead is a major residue component, as reported by Bashinski,[21] and as must be the case if antimony is found in the residue from ammunition with antimony-free primer, as reported, for example, in the Gulf General Atomic work.[15]

Only small spherical particles were found embedded in the surface of partially burned smokeless powder, and nondescript particles have not been observed on any of the large particles examined. This is consistent with a proposed ignition mechanism in which primer combustion produces hot globules of molten inorganic salts that contain the lead, antimony, and barium of the primer charge.[28] These hot globules then become embedded in the surface of the smokeless powder propellant particles (which are spheres or disks about 0.1 cm in diameter, composed of nitrocellulose, often a large fraction of nitroglycerine, and about 1% diphenylamine stabilizer, with an outer coating of carbon that is added to provide clean combustion). Small pellets of nitrocellulose are known to have higher ignition temperatures than large pellets; therefore, it is plausible that some of the small remnants of the initial smokeless powder particles are not ignited and collect spent primer globules on their surfaces.

Many residue particles deposited on the hand have nondescript morphologies, which makes it difficult to distinguish them from composite environmental particles by appearance alone. These particles lack symmetrical or highly ordered structure and do not have smooth surfaces. In this work, each nondescript particle studied contained some or all of the elements lead, barium, or antimony when analyzed by SEM with energy dispersive analysis, and each was stable under high-intensity SEM examination. Some appeared to be metal fragments, others as if they were composite mixtures produced by solidification of several inorganic compounds from small mixed melts. Although differentiation of these materials from environmental particles might be expected to be difficult, in practice, the microscopist has become sufficiently familiar with residue particles to recognize them by appearance plus elemental analysis.

There are definite differences in the types of particles that tend to be produced by different types of guns and ammunitions. For example, semiautomatics tend to deposit very large partially burned smokeless powder particles on the hand together with the host of smaller particles observed for other guns. The smokeless powder particles deposited by worn revolvers tend to be smaller than those produced by semiautomatics, but are otherwise similar.

Residue particles from the brands of .22 caliber ammunition with primers that lack barium and antimony tend not to contain these elements. However, the criminalistic value of this information is limited because a few residue particles from ammunition have been observed to contain some antimony or barium. Conversely, residue particles from primers that contain lead, barium, and antimony often produce only lead X-ray fluorescence.

Therefore, it is unlikely that guns and ammunition can be readily identified by current SEM analysis, but it is possible that future refinements might modify this conclusion.

B. Handblanks

In the limited examination of handblanks reported here, there was no difficulty in distinguishing handblank particles from gunshot residue. Although contaminants were found in the same size range as gunshot residue particles, most contaminant particles had characteristic features quite distinct from gunshot residue. For example, few had heavy metals, except for particles produced by various metal working processes, and these had shape and combinations of elements that were distinctive of the particular process. Judd and co-workers[3] surveyed contaminant particles found on the clothes of industrial workers and found a direct correlation between the elemental content of the particles and the occupation of the subjects. The topography and shape of contamination particles were further identifiable with job classification. Another source of data on environmental particles is the Particle Atlas.[29] In this document, particle properties that are useful for identification of unknowns are listed, and optical and SEM micrographs are given of an extensive range of particulate matter covering the substances that are representative of environmental contamination. All the materials included in the Atlas can be distinguished and identified by their microscopic properties. Most have characteristic structure, e.g., smooth crystal faces, that permits unique identification.

Biological materials, e.g., pollens and diatoms, have highly ordered structures that distinguish them from other materials. SEM micrographs of many environmental particles resemble those of the nondescript gunshot residue particles and a few of them contain lead. Several common lead pigments resemble nondescript gunshot residue: chrome yellow has lead, chromium, and iron; lead white has lead and iron; and naples yellow contains lead antimony, iron, aluminum, and silicon.[29] At high SEM magnification (10,000 ×), the latter was observed to be crystalline, but this is the only feature that distinguishes it from some types of residue. As mentioned earlier, another substance that might be confused with residue is automobile exhaust emission (Figure 9), which can contain spherical particles of lead, sulfur, silicon, calcium, vanadium, iron, and nickel.[29] (A large number of exhaust particles were examined during this study, all of nondescript shape with significant bromine content.) Some glass beads contain barium, iron, calcium, and silicon in spherical particulate form, and red lead and some electrical insulation materials contain lead and iron. Spherical particles that range from 3×10^{-4} to 3×10^{-3} cm are rather common. Many spray processes form them; for example, sprays of molten metals or molten salts usually solidify into such spheres. Plastics, aerosol sprays, oil soot, coal fly ash, and pollen particles often assume this shape. Therefore, elemental analysis is essential if these particles are to be distinguished from gunshot residue. It is apparent that the simultaneous presence of lead, antimony, and barium as major constituents of particles from 3×10^{-4} to 10^{-1} cm is highly uncommon for environmental particles, but is frequently observed in gunshot residue.

It is much more difficult to justify a conclusion that a handblank specimen contains no gunshot residue particles at all than to establish the presence of at least one or more gunshot residue particles in a specimen that contains many residue particles. If every residue particle on a specimen must be counted for quantitative purposes, then a large amount of effort must be expended in covering the total area of the specimen. It was found convenient to scan the specimen stage with the fast TV scan mode at about 100 × magnification, then increase magnification as required after a particle of interest was located. The X-ray analysis is then performed over a time interval sufficient to provide a signal-to-noise ratio of about 10:1 in the X-ray spectrum. This requires about 10 to 100 sec if the particle consists mainly of heavy metal. The SEM beam is rastered in the measurement; thus, the X-ray analysis is averaged over the recorded surface. If the particle under study is believed to be nitrocellulose, care is taken to minimize electron beam current in order to avoid particle destruction. Under these circumstances, it is essential to raster the beam to avoid excessive local heating. Unfortunately, the amount of X-ray signal is insufficient to permit high-resolution X-ray imaging. Therefore, it is not possible to locate residue particles directly by merely making an X-ray micrograph of the entire sample specimen at high resolution.

Most handsamples taken immediately after firing could be identified rapidly by a microscopist familiar with gunshot residue analysis. Residue from a Colt .22 revolver, for example, could be identified in less than 15 min; a careful search of an unknown handblank would require about 1 hr.

These times apply to the examination of specimens collected by repeatedly pressing a 2.5-cm-diam aluminum disk covered with an adhesive layer against the surface of the web area of the hand. More time would be involved if it were desired to compare the amount of residue on the back of the hand with the amount on the palm because all particles on the disks would have to be identified.

Results of the blind test of the analysis procedure with randomly mixed handblanks and firing samples indicated that the method has excellent potential for successful application. That 31 randomly mixed firing and handblank specimens were identified correctly can be compared with the results obtained in the Gulf General Atomic work,[15] which relied on detection by neutron activation analysis. In order to make the comparison, we established a 1% level of confidence criterion for the antimony/barium threshold; i.e., the threshold was fixed such that no more than 1% false positives were obtained for handblanks using their group (A) with low occupational exposure. (The results would be less favorable for the other groups.) Then, a practical threshold condition would be that the specimen contains more than 1.0 μg barium and 0.1 μg antimony. For their .38 revolver data, 60% of the firing handsample analyses would be false negative, and for .22 caliber guns, 81%.

CHAPTER VI. CONCLUSIONS

Particle analysis techniques provide much more information about identification of gunshot residue than the conventional analytical techniques that measure the microscopic concentration of elements. By combining the morphological information of the microscope with elemental analysis by X-ray fluorescence, scanning electron microscopy provides highly reliable identification of residue particles. Since the method is moderately insensitive to low concentrations of elements, homogeneously distributed lead, antimony, and barium hand contaminants are not detected, even though their total weights integrated over the hand are appreciable. Therefore, the particle analysis techniques should be reliable in situations where conventional methods fail as the quantity of residue approaches the background level. Most guns commonly encountered in criminalistics work can be expected to deposit many small particles; therefore, it should be possible to detect residue that remains an appreciable time after firing. The analysis procedures are sufficiently rapid for routine case work, and a typical specimen can be conveniently collected on an adhesive layer that is used with such other detection procedures as molecular luminescence. A firing handsample can be analyzed in 10 to 20 min, and a handblank, i.e., no residue present, can be identified in no more than 1 hr by an experienced analyst. The electron micrographs and X-ray spectra that are obtained are ideally suited for presentation in a court of law; the characteristics of residue particles are clear to the layman and should be highly convincing to a jury.

The method clearly provides the potential for significant improvement of gunshot residue detection; however, a number of aspects of the methodology need to be investigated before it can be accepted as an effective working tool. The persistence of particulate residue has not been established, and any successful methodology must detect residue long after a firing event, rather than immediately after, as in the test firing situations reported. It is expected that the micron-size particles should be retained well by the skin because of the large surface-to-mass ratio, but this hypothesis must be tested. Only a limited number of handblanks have been examined; therefore, effective use of the method by criminalistics laboratories must await thorough examination and classification of common contaminant particles that might be confused with residue. Then, optimum criteria can be established for evaluation of suspected residue specimens. Careful evaluation of residue particles produced by different guns, different ammunition, and residues issuing in different directions from guns might provide additional important criminalistics information. For example, it is already apparent that large particles of partially burned smokeless powder issue from the muzzle of "clean" revolvers, but do not vent significantly from the gap between the cylinder and barrel. This could be useful in differentiation of gunshot residue on the hands of a person standing along the line of fire from that on the hands of the person firing the gun.

Several criminalistics laboratories already have, or could afford to have, SEM equipment. However, the technique is expensive in equipment and demands too much operator specialization to be practical for the more numerous smaller local criminalistics laboratories. Therefore, there remains a strong demand for low-cost detection methods, even if they are not as definitive. The smaller laboratories might use the current elemental analysis methods, e.g., color tests,[21] flameless atomic absorption spectroscopy,[30] and molecular luminescence spectroscopy,[31] for presumptive tests to determine whether or not a suspect should be detained. If the test results were positive, then the remaining sample might be sent to a larger regional or national laboratory for confirmation by SEM (for court use). It has already been proven possible to collect residue handsample specimens on an adhesive layer and divide the layer such that one-half serves for screening analysis by molecular luminescence detection of lead and antimony and one-half is reserved for nondestructive analysis by SEM, provided the screening analysis is positive.

NOTES

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GLOSSARY

ADP. Ammonium dihydrogen phosphate.

ANTIMONY SULFIDE. A fuel in primers and an inorganic compound of formula Sb_2S_3.

AUTORADIOGRAPHY. A method for examining the spatial distribution of elements by making them radioactive, and then recording the radiation by placing the surface of the object of interest in close proximity to a photographic emulsion.

Ba. Barium.

BARIUM NITRATE. An oxidizing agent and major component of most modern primers. It is an inorganic compound of formula $Ba(NO_3)_2$.

BREMSSTRAHLUNG. (German: braking radiation.) A continuous spectrum of X rays produced by conversion of the kinetic energy of electrons as they are decelerated (braked) by the material through which they are traveling. The X-ray emission lines (X-ray fluorescence) of elements, that are due to transitions between energy levels of the inner electrons of an atom, are generally seen above a background of continuous radiation, of which Bremsstrahlung is the principal component.

Br. Bromine.

Ca. Calcium.

cal. Calorie.

cm. Centimeters.

CRT. Cathode ray tube.

Cu. Copper.

COULOMBIC. Due to electrostatic energy.

diam. Diameter.

EDAX. Trade name for energy dispersive X-ray analysis.

ENERGY DISPERSIVE X-RAY FLUORESCENCE DETECTION. The X rays emitted from a sample are detected by a semiconductor crystal that produces current pulses of amplitude proportional to X-ray energy. The energies are indicative of the element excited.

eV. Electron volts. The energy required to raise the potential of one electron by one volt (1.6×10^{-19} Joule).

Fe. Iron.

FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY. A standard analytical method for high-sensitivity elemental analysis. Compounds are decomposed into their separate atoms, and the amount of excitation light absorbed by each element is used for quantitative analysis.

g. Gram.

HANDBLANK. A specimen obtained for gunshot residue analysis from the hand of a person who has not fired a gun.

IITRI. Illinois Institute of Technology, Research Institute.

IMMA. Ion microprobe mass analyzer.

ION. Charged atom.

K. Potassium.

K. Designation for the X-ray fluorescence line generated when an electron in an outer shell makes a transition to a vacancy in the first or inner (K) electronic shell.

L. Designation for the X-ray fluorescence line generated when an electron in an outer shell makes a transition to a vacancy in the second (L) electronic shell.

LiF. Lithium fluoride.

LEAD STYPHNATE. The explosive initiator, and a major component of most modern primers, lead styphnate is an organometallic compound of formula $C_6HO_8N_3Pb$.

LITHIUM DOPED SILICON X-RAY CRYSTAL. A solid-state detector that converts X rays into electrical pulses with current proportional to X-ray intensity.

mm. Millimeter.

µg. Microgram.

M. Designation for the X-ray fluorescence line generated when an electron from an outer shell makes a transition to a vacancy in the third (M) electronic shell.

MOLECULAR LUMINESCENCE SPECTROSCOPY. An analytical method for detection and quantitative analysis of molecular species, using measurement of the spectral distribution and intensity of the light emitted by a molecule that results from excitation of electrons.

NEUTRON ACTIVATION ANALYSIS. An analytical technique used for sensitive quantitative elemental analysis. The method uses neutrons to make radioactive isotopes of elements in a specimen, and the resulting radiation emitted by the induced radioisotopes is measured.

Ni. Nickel.

PARAFFIN CAST. A traditional gunshot residue removal method in which warm melted paraffin is applied to a hand, and the resulting cast is removed, with residue particles adhering to the paraffin.

Pb. Lead.

PLASTIC FILM CAST. Solutions of cellulose acetate are applied to the hand. The resulting film is removed, along with gunshot residue particles.

S. Sulphur.

Sb. Antimony.

SECONDARY ELECTRON. A low-energy electron ejected from a specimen surface when a high-energy electron beam hits the sample. Secondary electrons are used to create the image produced by the scanning electron microscope.

SEM. Scanning electron microscope.

Si. Silicon.

SIGNAL-TO-NOISE. The peak signal intensity to the random fluctuations in the background continuum intensity.

SMOKELESS POWDER. The propellant used in modern commercial ammunition. It consists of particles of nitrocellulose, often incorporating nitroglycerine.

SPUTTER. Ejection of atoms from a surface under bombardment by ions or electrons.

Ti. Titanium.

Zn. Zinc.

END