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Glass-Containing Gunshot Residue Particles: A New Type of Highly Characteristic Particle?

ABSTRACT: In 0.22 caliber rimfire ammunition, the primer often contains lead or lead and barium compounds. As residues from these primers do not contain lead, barium, and antimony, they cannot be uniquely classified as gunshot residue (GSR) under ASTM designation E 1588-95. In many types of 0.22 caliber rimfire ammunition, the cartridge contains a primer sensitized with glass. In this paper we describe a previously unreported type of GSR particle consisting of glass fused with other primer components. As there appear to be few potential environmental or occupational sources of particles composed of lead and barium compounds fused to glass, particularly borosilicate glass, these particles may have high evidential value. Scanning electron microscopy with energy dispersive X-ray detection (SEM-EDX) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were evaluated for the characterization of glass-containing GSR particles. The occurrence of glass-containing GSR particles was established in the residue from various brands of 0.22 caliber ammunition, and several sub-types were identified.

KEYWORDS: forensic science, gunshot residue, 0.22 caliber ammunition, frictionator, glass, borosilicate glass, scanning electron microscopy, time-of-flight secondary ion mass spectrometry

Published studies on the analysis of primer-derived gunshot residue (GSR) are primarily concerned with particles formed from the melt or vapor phase and deposited on the shooter's hands (1–5). GSR particles may also be deposited on hands or clothing from contact with a firearm or fired cartridge case (6–8).

The detection of primer-derived GSR is conventionally performed using scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDX), a technique that combines excellent imaging capabilities with the ability to determine the gross elemental composition of these particles. EDX detectors equipped with beryllium windows do not detect elements of atomic number less than 11 (sodium) due to absorption of their low-energy X-rays. However, detectors with thin polymeric windows minimize window absorption, allowing the detection of elements with atomic numbers as low as 4 (beryllium). A scanning electron microscope equipped with such a detector was used in this study to obtain additional information from the light elements present in GSR particles.

Generally, GSR particles derived from centerfire ammunition have a distinct morphology and contain lead, barium, and antimony. Under ASTM designation E 1588-95 (9) such particles are deemed to be unique, however a recent paper by Torre (10) suggests the word unique is unwarranted in light of the occurrence of environmental particles with similar compositions. Most 0.22 caliber rimfire ammunition produces residues containing lead only or lead and barium. Particles with these compositions may originate from other sources such as fireworks (11) and other environmental or occupational sources (6,12,13) and, according to ASTM designation E 1588-95, cannot be classified uniquely as GSR. Such particles are considered to be of lower evidential value than particles containing lead, barium and antimony.

In addition to lead, barium, and antimony, GSR may contain other elements that might be of significance, including silicon (1,3,14–18) and boron. Possible sources of silicon include glass and calcium silicide, both used as frictionators in cartridge primer mixtures (6,14,15,19). A possible source of silicon and boron is borosilicate glass, also used as a frictionator (20). It is our belief that in the GSR from 0.22 caliber ammunition, certain types of particles rich in silicon are composed of glass fused with other primer-derived material. The occurrence of these particles in GSR does not appear to have been reported in the literature.

In a previous study (21), it was shown that time-of-flight secondary ion mass spectrometry (TOF-SIMS) can be used in GSR analysis. TOF-SIMS is a surface-sensitive analytical technique (monolayer detection) that can provide images (including elemental maps) of GSR particles. It has excellent detection limits (down to ppb level) for all elements (hydrogen-uranium) (22,23). TOF-SIMS can also be used to depth profile individual GSR particles, a capability that allows the spatial distribution of elements within a particle to be determined.

The aims of the present study were to characterize glass-containing GSR particles by SEM-EDX and TOF-SIMS, to establish the occurrence and variation of these particles in various types of 0.22 caliber ammunition, and to explore the occurrence of these particles on hand and wound samples.

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Materials and Methods

Standard Glass Samples

Standard reference material (SRM) 621 (soda-lime container glass) and SRM 93a (12.5% B_2O_3 borosilicate glass) were purchased from NIST, Gaithersburg Maryland. Small pieces of each standard sample were broken off, fragmented (50 to 200-μm particles), and transferred onto indium foil mounted on a SEM stub.

Recovery of Glass Particles from Unfired 0.22 Cartridge Cases

Following the removal of the projectile and propellant, the procedure documented by Wallace (18) was followed for desensitizing the primer mixture. The cartridge was immersed in a 2:1 solution of acetone and water for 48 h in a disposable polypropylene container. The mixture was placed into an ultrasonic bath for 20 min and the interior of the cartridge case rinsed with a jet of water. The glass particles were allowed to settle and the liquid layer decanted. The recovered glass particles were rinsed with concentrated nitric acid, water, and ethanol. For TOF-SIMS analysis, the particles were transferred onto indium foil, overlain with a copper reference grid and mounted on a SEM stub.

Collection of Gunshot Residues from Fired Cartridge Cases

GSR particles were transferred onto a stainless steel plate by tapping the inverted fired 0.22 caliber cartridge case on the plate. An indium foil mounted on a SEM stub was then lightly pressed onto the particles. Particles were also collected in a similar manner on adhesive carbon tape.

Collection of Gunshot Residue from Hands

GSR particles were collected from the hand of a shooter by tape-lifting from rear, upper surfaces of the firing hand that had not been in contact with the firearm. The firearm used was a Smith and Wesson 0.22 caliber LR 5-in. barrel model 617 revolver. Winchester Power Point 0.22 caliber LR ammunition was used.

Collection of Gunshot Residues from Wounds

Particles were collected from the wound margins by dabbing with double-sided adhesive carbon tape mounted on a SEM stub.

Measurement of Refractive Index

RI measurements were obtained using the immersion method with phase contrast microscopy and a GRIM apparatus (Foster and Freeman).

Instrumental Operating Parameters

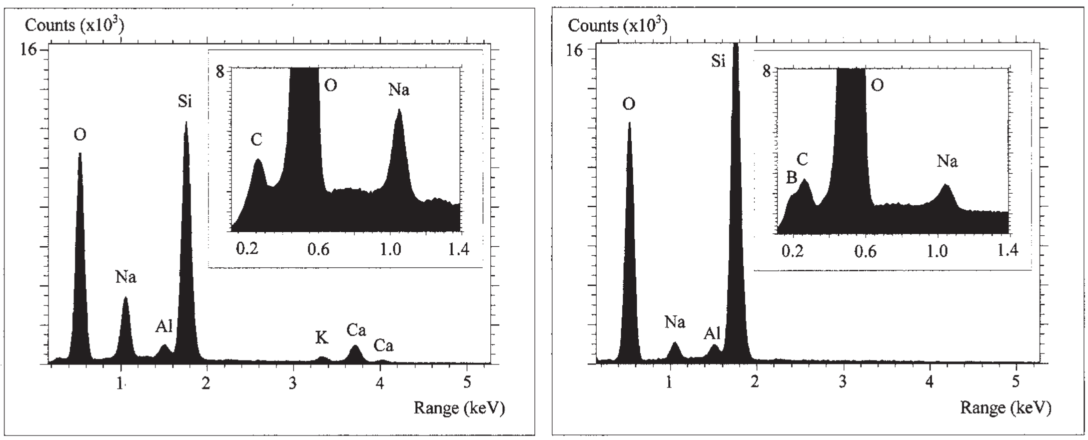
Scanning electron microscopy—Imaging and particle analysis was performed using an integrated SEM-EDX system consisting of a Cambridge Stereoscan 360 SEM and a Link eXL microanalysis system. The X-ray detector was an Oxford Link Pentafet fitted with an ATW2 window. Initial elemental analysis was performed at an accelerating voltage of 25 kV. Light element analysis was performed at 7-kV accelerating voltage. A field emission Camscan scanning electron microscope was also utilized for backscattered electron image acquisition. Particle samples were not coated unless stated.

Time-of-Flight Secondary Ion Mass Spectrometry—A Physical Electronics Inc. Models 2100 PHI Trift II™ TOF-SIMS equipped with a pulsed liquid metal $^{69}Ga^{+}$ primary ion gun (LMIG) was employed. The primary ion gun was operated at 25 kV energy, 600 pA beam current (DC value), and a pulse length of 20 ns. Surface etching was performed by switching the primary ion gun to continuous (DC) beam mode for controlled periods.

Results and Discussion

Analysis of Standard Reference Materials: SRM 93a (Borosilicate Glass, 12.5% B_2O_3), and SRM 621 (Soda-Lime Container Glass, Boron Free)

SEM-EDX Analysis—Standard glasses were analyzed to demonstrate the ability of the EDX detector fitted with a thin polymeric window to detect the component elements. Figures 1*a* and 1*b* show the EDX spectra from the standard soda-lime and borosilicate glasses. The two glass types can be distinguished by the presence of boron, which appears as a shoulder on the carbon peak, and the differing oxygen, sodium, aluminum, silicon, potassium, and calcium profiles. The source of the carbon peak is believed to be from oil back-streaming into the SEM chamber from the rotary backing pump.



(a) (b)

FIG. 1—(a) *SEM-EDX spectra from SRM 621 at accelerating voltages 25 and 7 kV (inset).* (b) *SEM-EDX spectra from SRM 93a at accelerating voltages 25 and 7 kV (inset).*

The signal-to-noise ratio for boron improved with lower accelerating voltage; however, the SEM backscattered electron (SEM BSE) image quality decreased. An accelerating voltage of 7 kV was therefore chosen for light element analysis to permit adequate imaging of GSR particles. The samples were not carbon, coated as the increased carbon signal precluded the detection of boron.

TOF-SIMS Analysis—The presence of boron in SRM 93a was clearly evident from the TOF-SIMS results (Fig. 2). Additional elements detected were lithium, sodium, aluminum, silicon, potassium, calcium, and barium. Note that the presence of peaks due to minor isotopes confirms the elemental assignments. For example, in addition to the peak at 11 amu due to the major isotope of boron, a peak due to ^{10}Boron at 10 amu is present in the appropriate relative abundance.

An initial surface analysis of SRM 621 revealed that elements detected in SRM 93a were also present in SRM 621 but at different levels (refer to depth profile results).

Depth profiles of both SRM 93a and SRM 621 were acquired (Figs. 3 and 4) by switching the primary ion beam to DC mode for controlled periods of time between successive data acquisitions. The ability of TOF-SIMS to analyze as a function of depth allows visualization of the change in composition from the surface to the bulk of the particle. Results indicated that the elements selected for profiling provided a constant signal, and thus variations in the glass matrix were negligible.

Direct visual comparison between the profiles allows effective discrimination between the two standard samples, particularly in the levels of boron. Other elements that could be used to discriminate between the samples were potassium, calcium, aluminum, magnesium and zirconium. Figure 5 represents a bar chart, which further illustrates the differences between the elemental composition in the two standards.

These results demonstrate that due to superior detection limits, TOF-SIMS provides additional elemental information that SEM-EDX is not capable of providing.

Analysis of Glass Extracted from Unfired Winchester 0.22 Caliber Cartridges

SEM-EDX Analysis—Glass particles recovered from unfired Winchester 0.22 caliber cartridges varied in size, with the majority ranging from 30 to 250 μm (Fig. 6*a*). SEM-EDX analysis of non-carbon-coated particles produced spectra (Fig. 6*b*) confirming their identity as borosilicate glass.

TOF-SIMS Analysis—Figure 7 represents secondary ion images (total ion) of typical particles from unfired Winchester 0.22 caliber ammunition that were analyzed by TOF-SIMS.

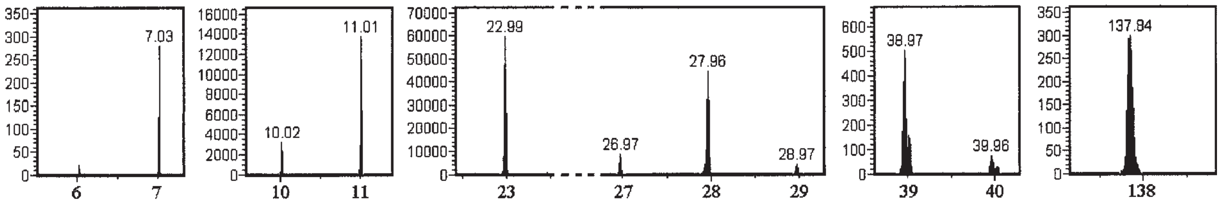


FIG. 2—*Selected mass range secondary ion mass spectra of SRM 93a. Lithium (7.03 amu), boron (11.01 amu), sodium (22.99 amu), aluminum (26.97 amu), silicon (27.96 amu), potassium (38.97 amu), calcium (39.96 amu), and barium (137.84 amu).*

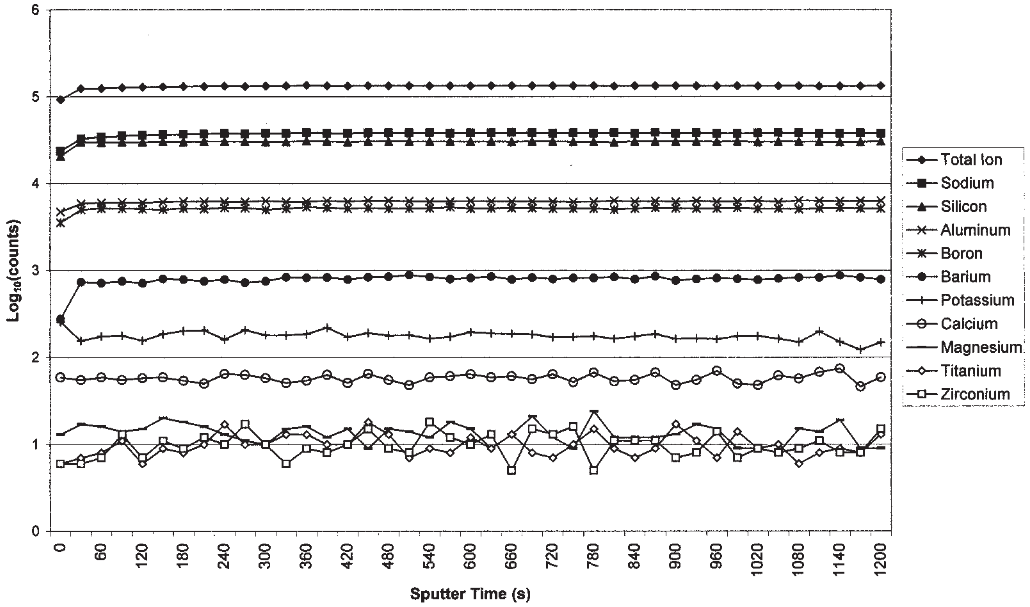


FIG. 3—*Depth profile of SRM 93a.*

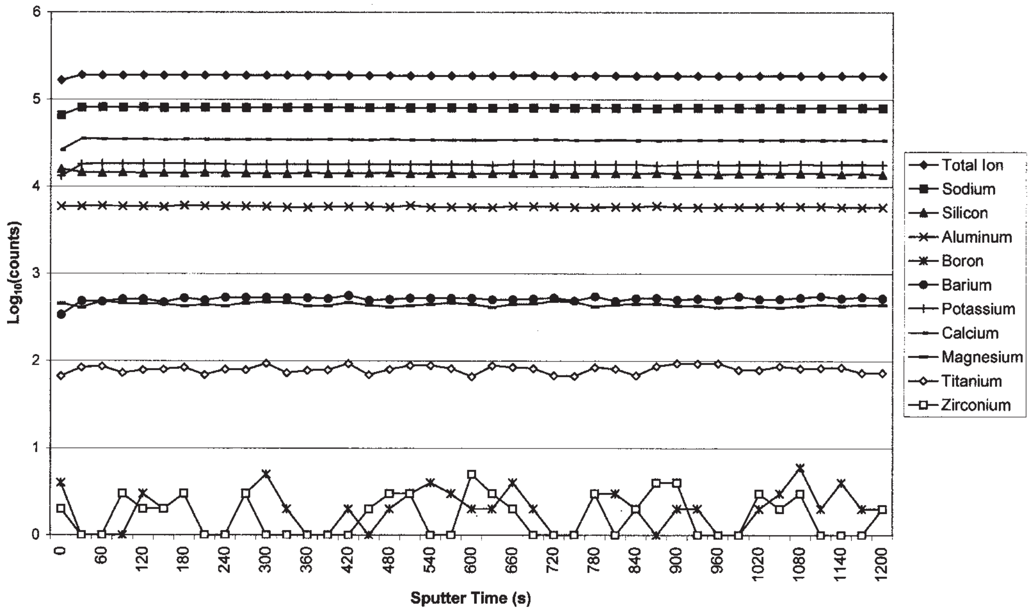


FIG. 4—*Depth profile of SRM 621.*

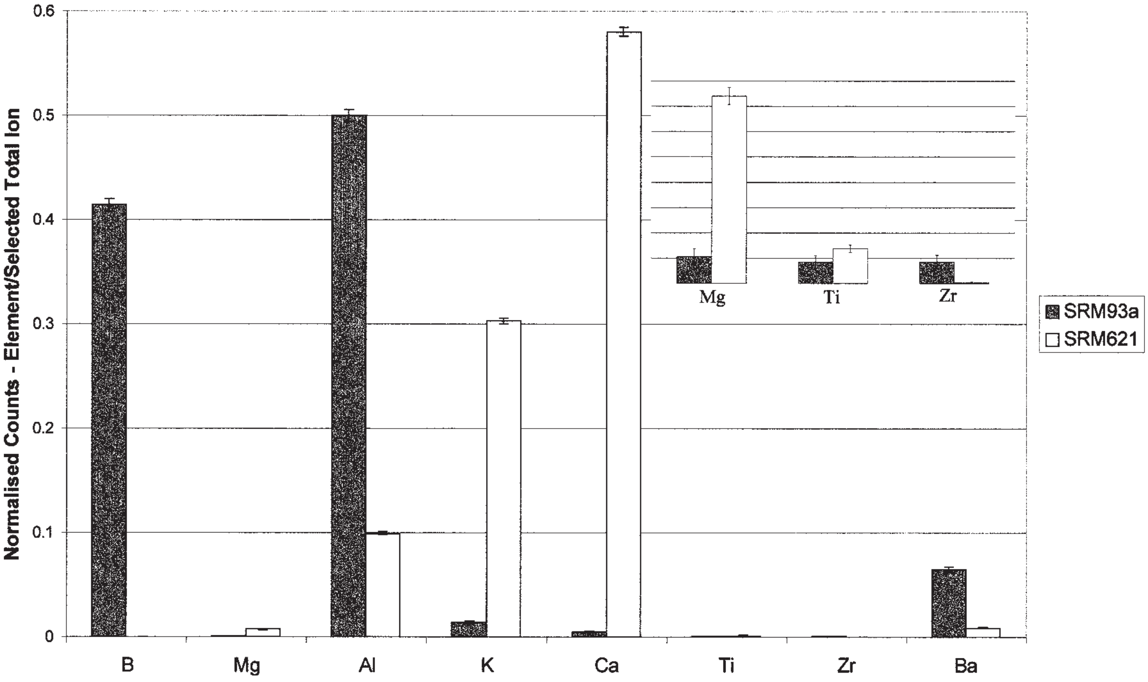


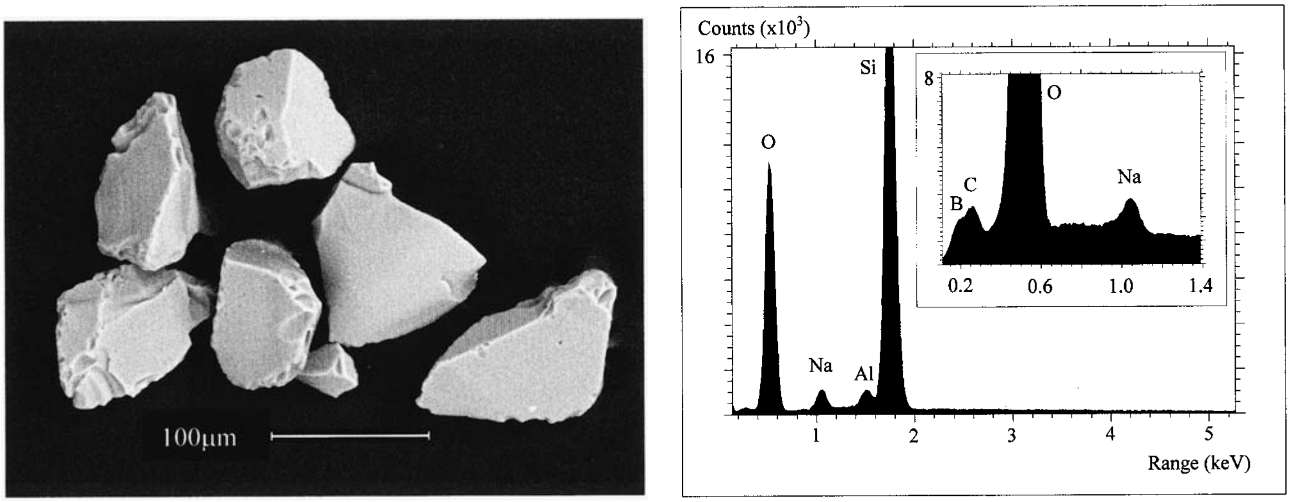
FIG. 5—*Selected elemental comparison between standard samples SRM 93a and SRM 621.*

Elements detected by TOF-SIMS included lithium, boron, sodium, magnesium, aluminum, silicon, potassium, calcium, magnesium, titanium, and zirconium. A depth profile of these elements is illustrated in Fig. 8.

Depth profiles of the unfired cartridge glass particles (Fig. 8) indicated that the elemental distributions within the particle were uniform. Results highlighted in Fig. 9 indicate that the cartridge glass particles and glass standard SRM 93a appear to be similar borosilicate glasses with marginal differences in potassium and calcium content.

Analysis of Gunshot Residue Recovered from Fired 0.22 Caliber Cartridge Cases

Identification of Glass-Containing GSR—Particles consisting of primer-derived compounds fused with glass were identified via the



(a) (b)

FIG. 6—(a) *SEM BSE image of borosilicate glass particles recovered from an unfired Winchester 0.22 caliber cartridge case (carbon coated).* (b) *SEM-EDX spectra from unfired Winchester 0.22 caliber primer glass at accelerating voltages 25 and 7 kV (inset).*

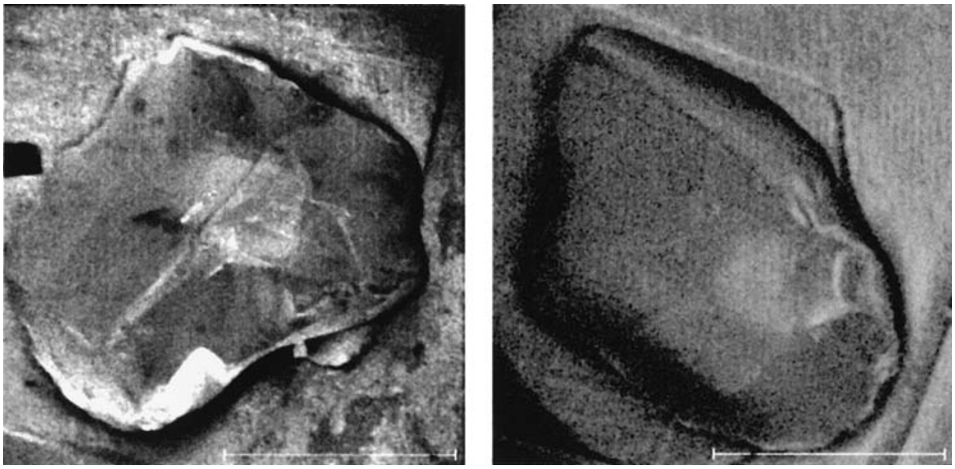


FIG. 7—*Secondary total positive ion images of typical particles analyzed by TOF-SIMS (scale: 100 µm).*

SEM BSE image in which bright regions represent high atomic weight primer residue and dull regions represent relatively low atomic weight glass (Fig. 10).

The particles ranged in size to 250 µm and exhibited a range of morphologies. The original fracture ridges present on the glass were smoothed to varying extents, indicating softening of the glass component during the formation of the particles. Accordingly, primer components (containing lead, barium, etc.) appeared to have combined with the glass to various extents ranging from significant ingress (Fig. 10*a*) to forming a surface coating (Fig. 10*b*). Most particles appeared to comprise a core of glass with a fused crust of primer-derived material. In some instances, discrete spheres of primer-derived residue were adhering to the particle surface (Fig. 10*c*). Some particles appeared to have fractured after formation, possibly during collection (Fig. 10*d*), thereby creating sharp fracture ridges.

Ammunition producing glass-containing GSR particles with exposed glass surfaces often also produced particles from which silicon was detected in the SEM-EDX spectra but did not exhibit exposed glass surfaces. It is assumed that for such particles the glass was either completely coated with, or extensively mixed with, the other primer components.

Compositional Analysis of GSR Recovered from a Fired 0.22 Caliber Winchester Cartridge Case by SEM-EDX and TOF-SIMS—The SEM BSE image (Fig. 11*a*) and the SEM-EDX spectra (Figs. 11*b* and 11*c*) show that the primer-derived lead and barium residues (bright region) are fused to a borosilicate glass core (dull region). Elements that produce X-rays at approximately 0.18 keV and therefore may interfere with SEM-EDX analysis of boron include sulfur, chlorine, molybdenum, and niobium. These elements are not present in glass at levels that would cause interference for the detection of boron. Sulfur and chlorine may be associated with the detection of GSR (3,18); however, the presence of these elements in surface contamination on exposed glass surfaces of glass-containing GSR particles would be identified by their K peaks in the 25-kV spectrum.

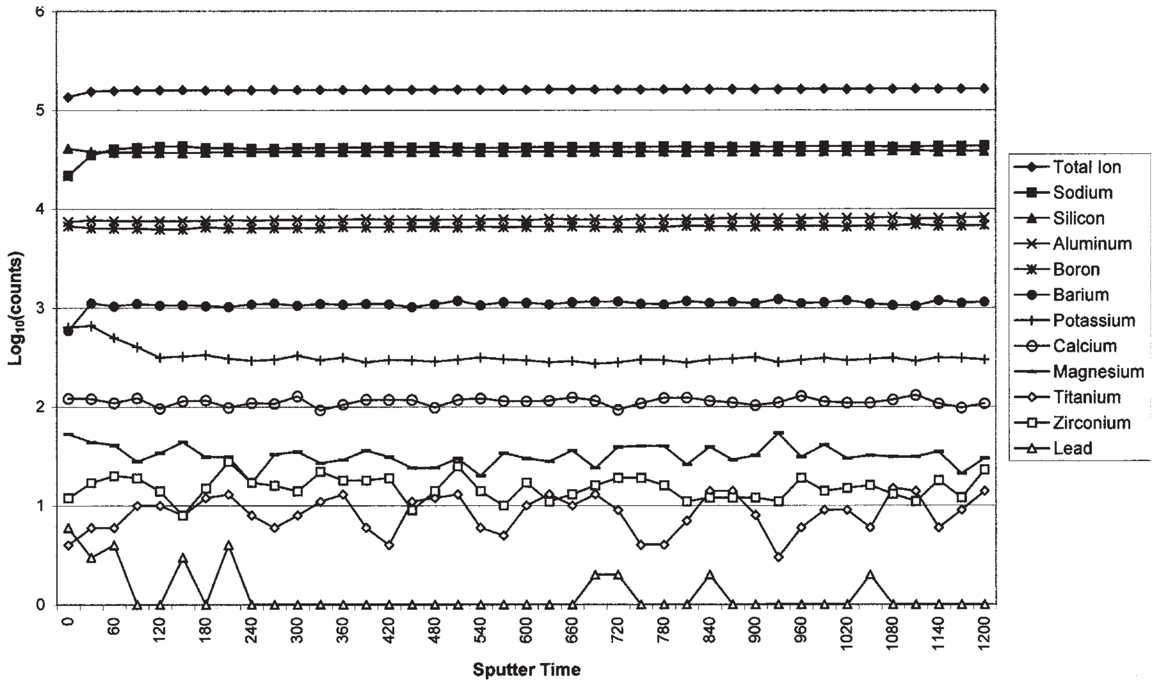


FIG. 8—*Depth profile of a glass particle extracted from an unfired 0.22 caliber Winchester cartridge case.*

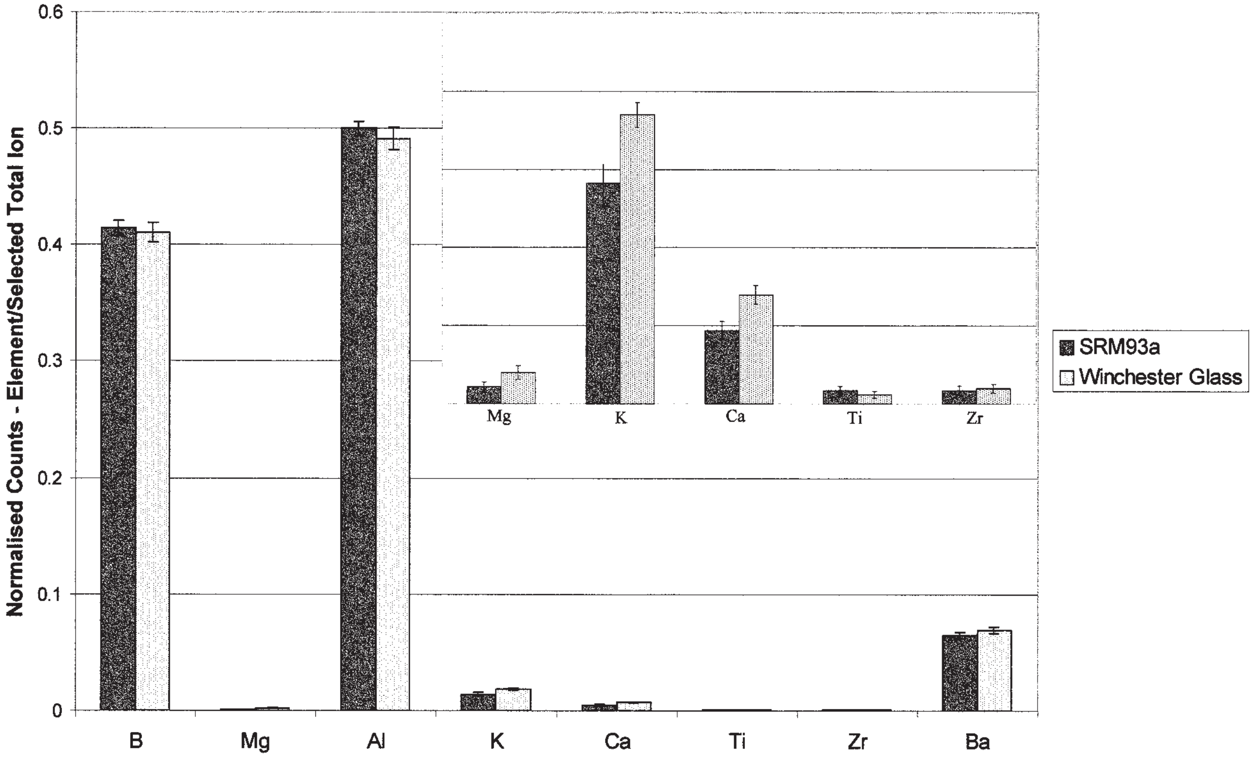


FIG. 9—*Comparison of profiled elements between SRM 93a and glass extracted from an unfired 0.22 caliber Winchester cartridge case.*

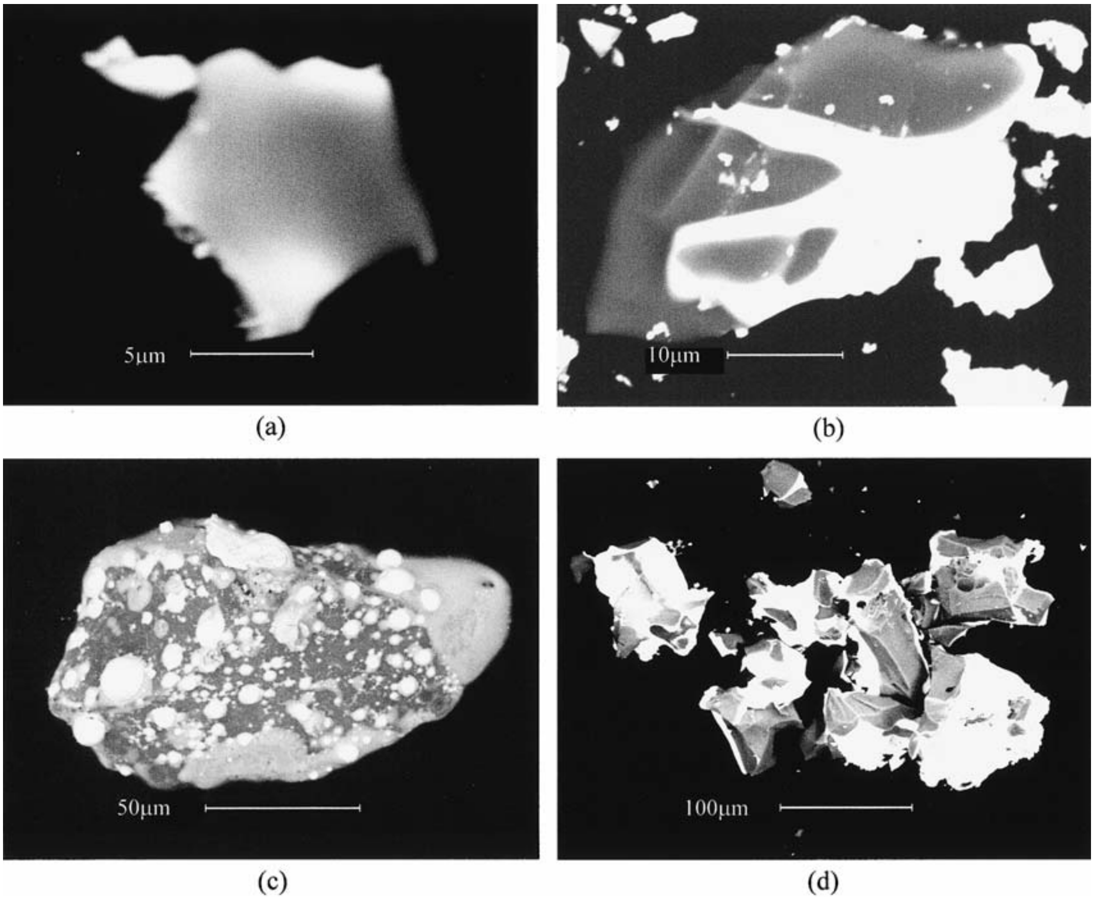


FIG. 10—*SEM BSE images of particles identified as primer-derived material (bright regions) fused to glass (dull regions):* (a) *Federal "Magnum";* (b) *Winchester "Power Point";* (c) *CCI "Mini Mag";* (d) *Winchester "Power Point Magnum."*

The spectra from the dull region were indistinguishable from those of the unfired Winchester glass (Fig. 6*b*). The EDX spectrum from the bright region (Fig. 11*c*) was typical of 0.22 caliber Winchester GSR (15,21).

TOF-SIMS was capable of providing additional elemental information and an indication that for this particle the extreme surface of the glass becomes chemically modified during firing to a depth of approximately 200 nm. An initial TOF-SIMS surface analysis was performed prior to any surface etching or depth profiling. Figure 12 represents the mass spectrum. Elements detected include boron, sodium, silicon, potassium, barium (138 amu), and lead (208 amu).

The secondary ion images (Fig. 13) illustrate the spatial distribution of the selected elements. As can be seen from the image for boron and from the mass spectral data (Fig. 12), the response for boron from the surface of the particle was extremely low. Furthermore, aluminum was not detected on the surface.

The entire surface of the particle was then subjected to ion etching over controlled periods. Previous experience (21) indicates that the rate of ion etching is approximately 0.2 nm/s. Therefore, in this procedure most of the lead and barium-rich residue remains intact. After a 600 s etch period, secondary ion mass spectra were reacquired. From the resulting mass spectra it was confirmed that lead and barium were dominant within the bright regions of the SEM BSE image, whereas boron, silicon, and aluminum were dominant within the dull regions. It was apparent that sodium, potassium, and calcium were distributed over the entire particle surface. The spatial distribution of elements after the surface etch is clearly illustrated in the secondary ion images (Fig. 14). The SEM BSE image is included for direct comparison with the selected elements. The mapping capability of TOF-SIMS allowed simple qualitative identification of the various regions of the GSR particle.

These analyses were followed by depth profiling within a 25 by 25 μm area of the glass region (dull SEM BSE image region). The resulting depth profile is presented in Fig. 15.

The depth profile indicates that a sputter period of about 1000 s is required before the composition within this region "levels out." It is informative to compare Fig. 15 with Fig. 8; only a short sputter period was required in the analysis of unfired glass before the elemental profiles "leveled out." This indicates that the surface of the glass particles becomes modified during the firing process. Compared to the unfired glass, the fired glass surface appears to have become richer in potassium, barium, and lead, but depleted with respect to zirconium, sodium, and calcium. An obvious conclusion is that the surface of the glass has absorbed elements (lead from lead styphnate; barium from barium nitrate) from the primer during firing.

SEM-EDX analysis was performed on the particle following the depth profile. A SEM BSE image was acquired to illustrate the effect of ion etching on the surface of the particle (Fig. 16). As previously described (21), it was possible to switch between SEM-EDX and TOF-SIMS without destroying the integrity of the sample.

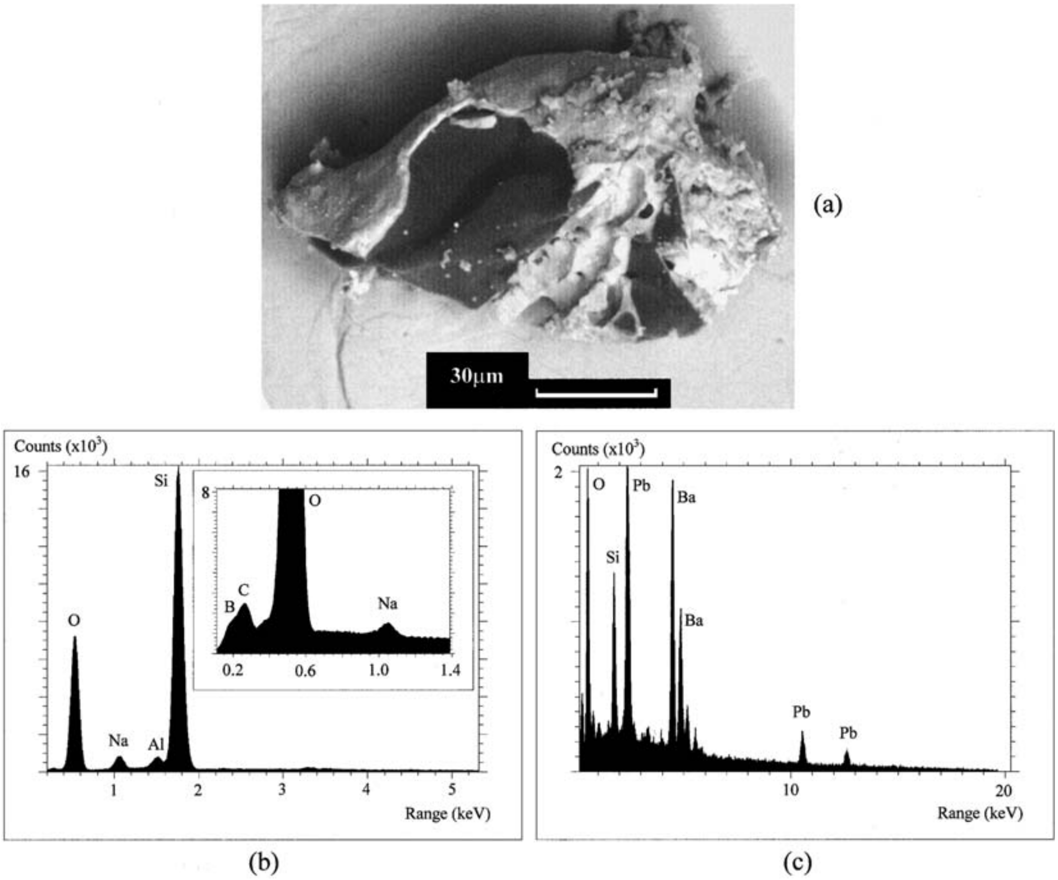


FIG. 11—(a) *SEM BSE image of a particle recovered from a fired Winchester cartridge case.* (b) *SEM-EDX spectra from the dull region at accelerating voltages 25 and 7 kV (insert).* (c) *SEM-EDX spectrum from the bright region at accelerating voltage 25 kV.*

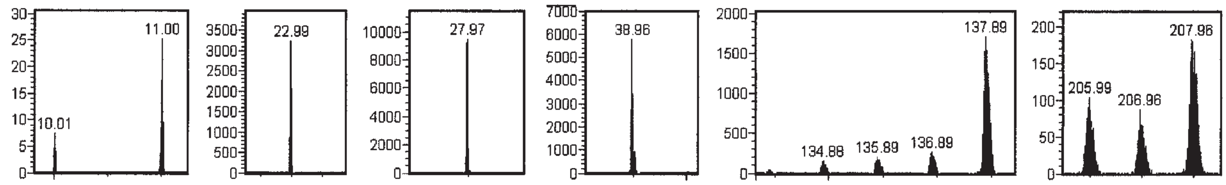


FIG. 12—*Selected mass range secondary ion mass spectra—initial surface analysis. Minor isotopes for boron, barium, and lead are depicted.*

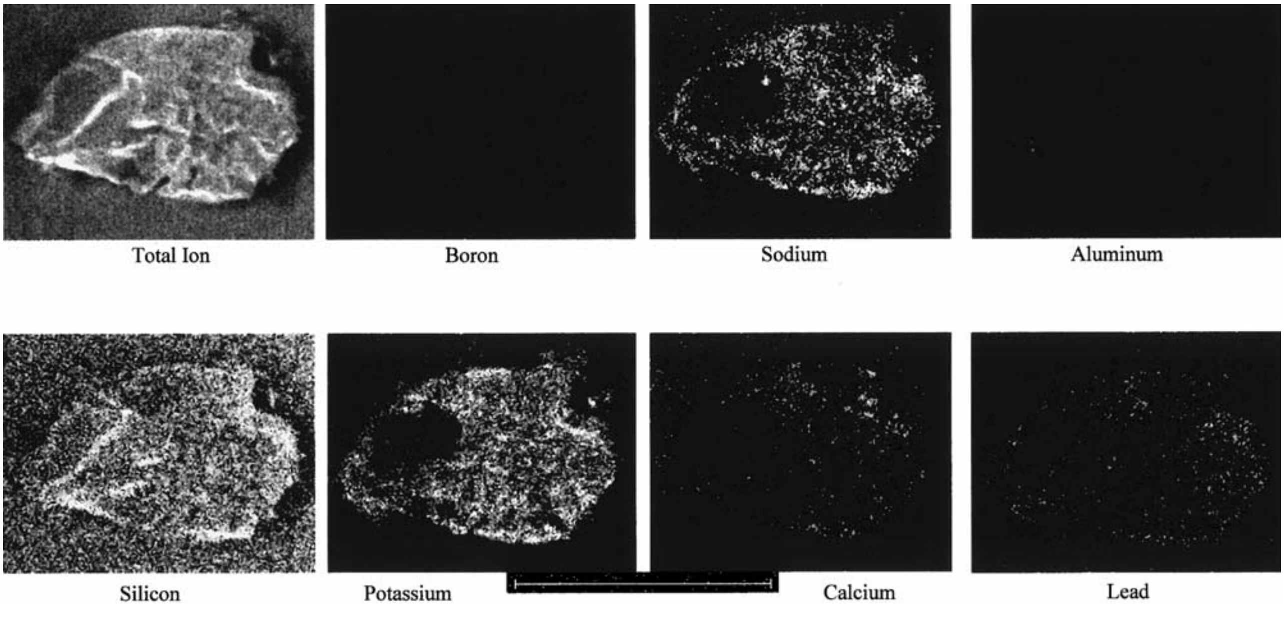


FIG. 13—*TOF-SIMS secondary ion images (scale: 100 μm).*

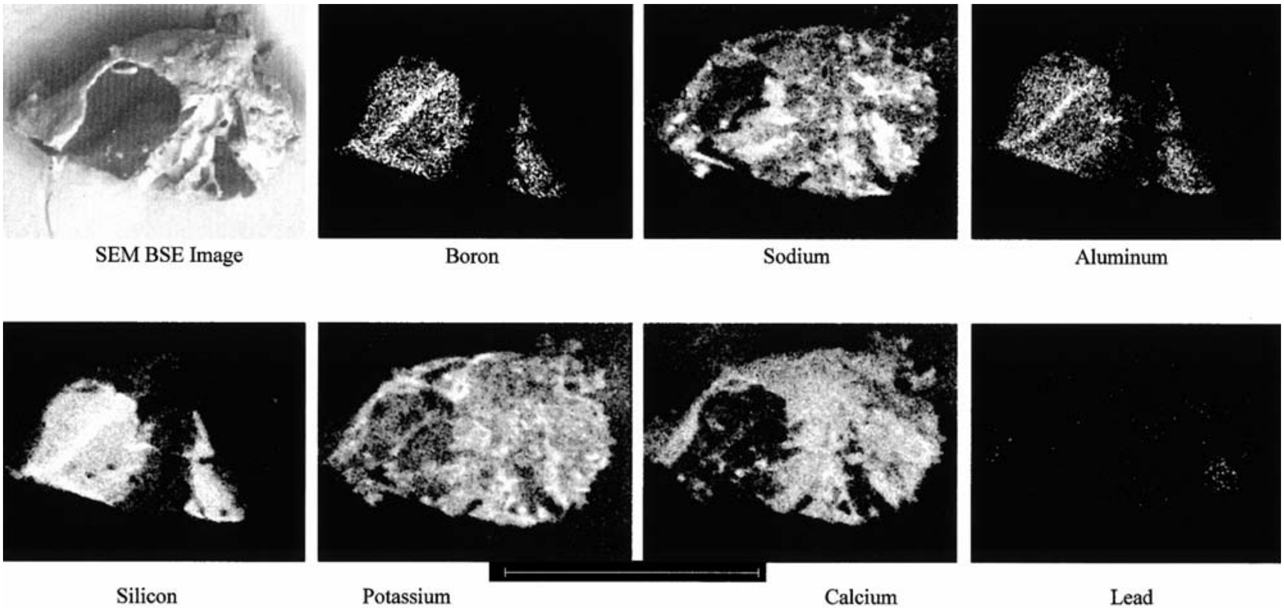


FIG. 14—*SEM BSE image and TOF-SIMS secondary ion elemental maps (scale: 100 μm).*

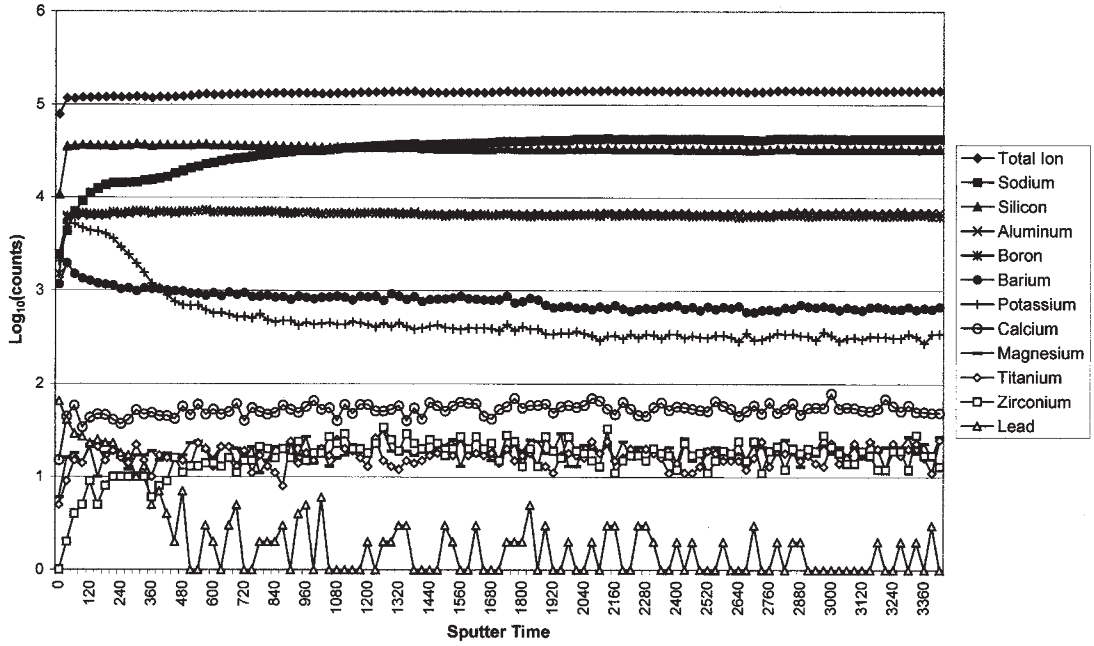


FIG. 15—*Depth profile acquired within the glass region.*

The SEM-EDX spectrum of the etched glass region of the particle, acquired at 7 kV (Fig. 17), included a gallium L peak, unresolved from the sodium peak, indicating some degree of surface impregnation of gallium. The detection of other light elements was unaffected.

The 25 by 25 μm ion beam etched square produced during depth profiling is clearly visible within the glass region (Fig. 16). Comparison between the pre- and post-TOF-SIMS analysis images demonstrates that the bulk of the analyzed particle remains intact and the overall morphology is unaltered. The non-destructive nature of TOF-SIMS makes it a highly attractive technique for forensic purposes. Following comprehensive TOF-SIMS analysis of the particle, it can subsequently be analyzed by other techniques.

Identification of Glass-Containing GSR Recovered from the Hand of a Shooter

Glass-containing GSR particles ranging in size from 2 to 100 μm were detected on samples collected from the hand of a shooter immediately after firing the test revolver using 0.22 caliber Winchester ammunition (Fig. 18). Imaging and analysis were performed on samples without carbon coating. The appearance of these parti-

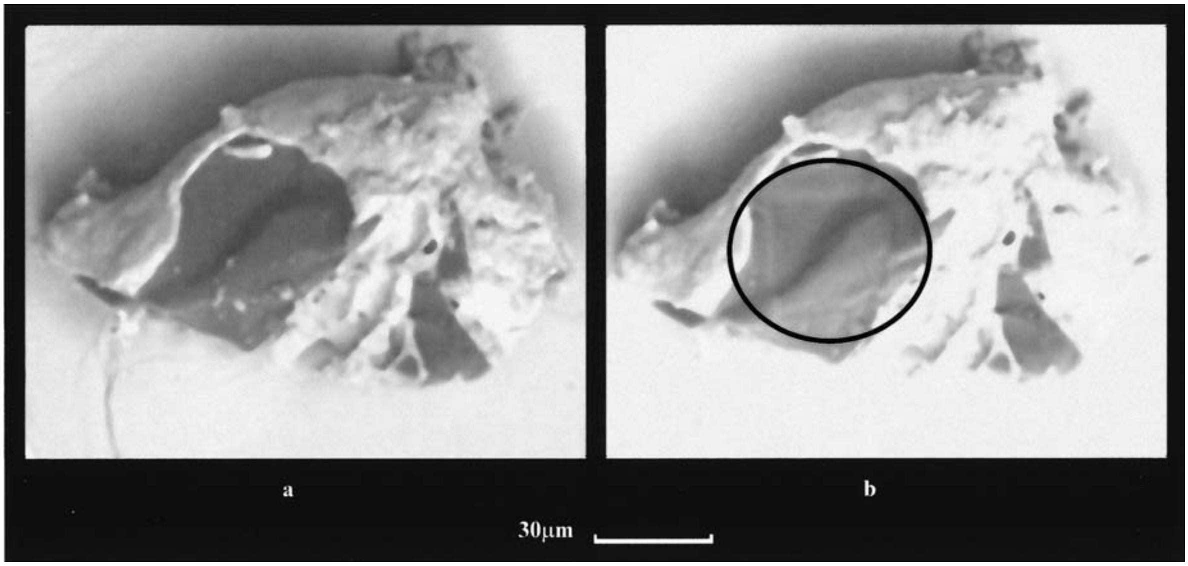


FIG. 16—(a) *Pre-depth profile and* (b) *post depth profile SEM BSE images of the analyzed particle. 25 by 25-µm etched profile square (circled) visible in (b).*

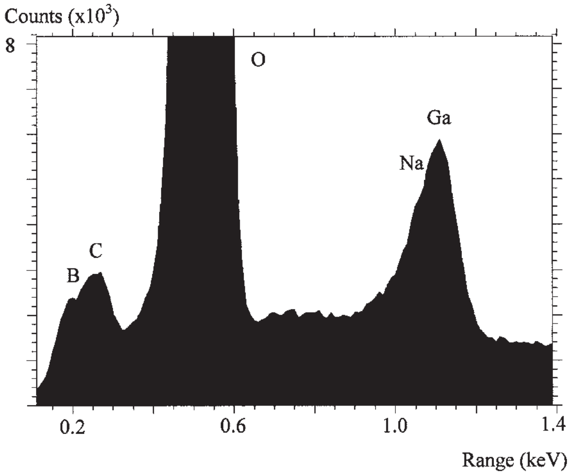


FIG. 17—*SEM-EDX spectrum from the etched glass region (7 kV).*

cles was consistent with particles recovered from fired cartridge cases (Fig. 10).

The appearance and SEM-EDX spectra of some larger particles indicated that the glass was extensively fused with residue of high barium content (Fig. 19). Boron was detected in the 7 kV spectrum, and at 7 kV and 25 kV the oxygen, sodium, aluminum, and silicon profile was characteristic of borosilicate glass. Low levels of lead were detected in the 25 kV spectrum taken from the bright region of the SEM BSE image.

In some particles containing silicon, no discrete glass surfaces were observed, indicating substantial incorporation of the original glass with other primer components (Fig. 20).

Significance of Glass-Containing GSR Particles in Casework

It is our opinion that the evidential value of GSR derived from lead and barium type 0.22 caliber primers is significantly increased when glass-containing GSR particles are also detected. Sources of particles containing lead, barium, or lead and barium include automotive mechanisms, paint, ink, fireworks, military incendiary compositions, and bearing metals (6,10–13). Glass fibre, and lead, barium and antimony compounds are listed as possible components of brake linings (24). Borosilicate glass and lead alloys are listed as possible components of composite friction materials in US patents (25,26), where these materials are designed for use in applications such as automotive brake linings. Lead and barium compounds, and glass are used as pigments and fillers in paints and plastics (27). It is also acknowledged that certain industrial power tool cartridges and blank cartridges produce residue indistinguishable from GSR (13,18,28). The particles described have morphology indicative of the fusion of lead and barium compounds with glass of varying viscosity. This suggests a high-temperature event, which realistically limits production of these particles to events such as an explosive discharge, ignition of fireworks or thermal fusion of brake linings (10). The use of elemental silicon and boron, but not glass, is reported in fireworks and military incendiary compositions (27,29–31). Glass has no obvious use in fireworks and is rarely used (31), hence, the use of relatively uncommon borosilicate glass in fireworks is unlikely. Brake linings may be a possible source of particles with composition similar to those described herein. Whether particles derived from brake linings would have morphology as described is unknown.

This paper indicates that glass-containing GSR particles may deposit on the hand of a shooter when firing a revolver. An earlier study (15) suggests that such particles are likely to be relatively large (>20 µm) and in low abundance compared to the smaller GSR particles produced. The impact of these two factors should be taken into account when making an assessment of the retention of GSR residues on the hands of shooters.

During the course of casework we have detected glass-containing GSR particles on samples taken from 0.22 caliber firearms and fired cartridge cases and on samples taken from the wounds of persons known to have been shot at close range with 0.22 caliber ammunition (Fig. 21). Glass-containing GSR particles have also been recovered from clothing and from the interior of a motor vehicle.

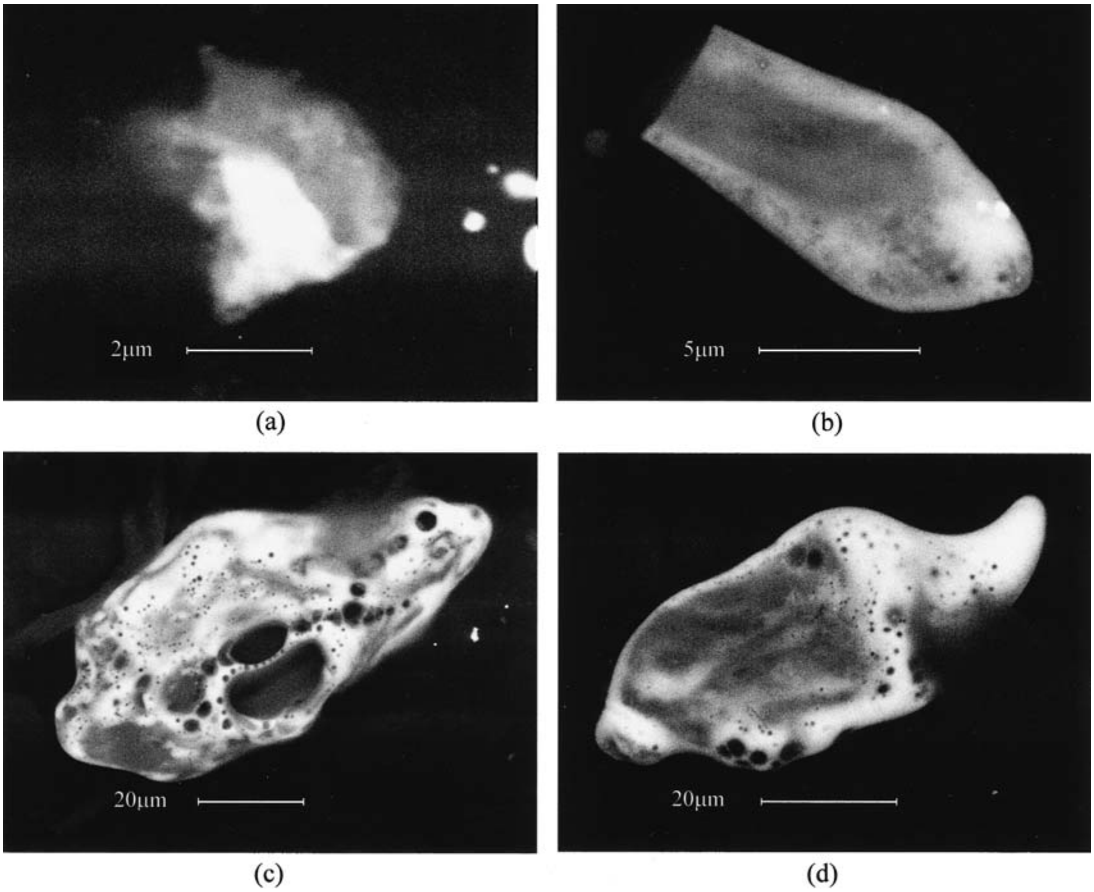


FIG. 18—*SEM BSE images of glass-containing GSR particles recovered from the hand of a shooter (Images c and d partially obscured).*

As described by Romolo and Margot (32), an important consideration for the chemical criminalist is whether GSR particles found on a specific surface "match" those from a putative source. In cases where recovered particles have exposed glass surfaces, analysis can provide a useful link. For example, the analysis of glass-containing GSR particles recovered from close range gunshot wounds might assist investigators to identify the brand of ammunition used if no cartridge case is recovered. It may also be possible to associate wound particles with particles recovered from persons, clothing, or surfaces that have been near the discharge or in contact with the fired cartridge case or firearm used to commit the offense.

It has been found that SEM-EDX may be of limited use for characterizing glass-containing GSR particles in casework samples that are overlaid with debris. Etching these particles using the TOF-SIMS instrument as described has revealed the underlying structure of these particles and permitted TOF-SIMS and SEM-EDX analysis, thereby providing a high degree of confidence in their classification as GSR.

SEM-EDX Survey of Residues Produced by 0.22 Caliber Cartridges and Ramset Power Tool Cartridges

Particles were recovered from fired 0.22 caliber cartridges representing a selection of ammunition types purchased in Australia (Table 1). Spectra were acquired from exposed glass surfaces and from the fused primer-derived material of uncoated, glass-containing GSR particles. Spectra were also acquired from uncoated glass recovered from unfired cartridge cases.

The majority of ammunition types produced GSR including particles comprising lead and barium residues fused to borosilicate glass. Apart from RWS "High Velocity", the borosilicate glasses analyzed were indistinguishable from the Winchester glass described previously. Refractive index measurements on glass from unfired Winchester and CCI cartridges were indistinguishable (nD 1.473). Three samples contained particles comprising lead, barium, and antimony residues fused to borosilicate glass. Samples from two brands (Lapua and Fiocchi) contained no glass.

One ammunition (RWS "High Velocity") produced a mixture of two particle types, lead and barium residues fused to a borosilicate glass of unusual composition (Fig. 22), and lead and barium residues fused to soda lime glass. Refractive index measurements of glass recovered from an unfired cartridge case confirmed the presence of two distinct glass types having refractive indices of nD 1.511 and 1.522. There was a strong correspondence between the spectrum from the unfired borosilicate glass (Fig. 23*b*) and the spectrum from the dull region of a particle from the fired cartridge case (Fig. 22*b*), indicating that this region was glass, substantially unaltered during firing. This GSR was of such peculiarity that it might be unique to this brand.

Two ammunition types, PMC "Zapper" and Remington "Hi Velocity" had differing composition between batches. Soda-lime glass spheres were recovered from one batch of unfired PMC "Zap-

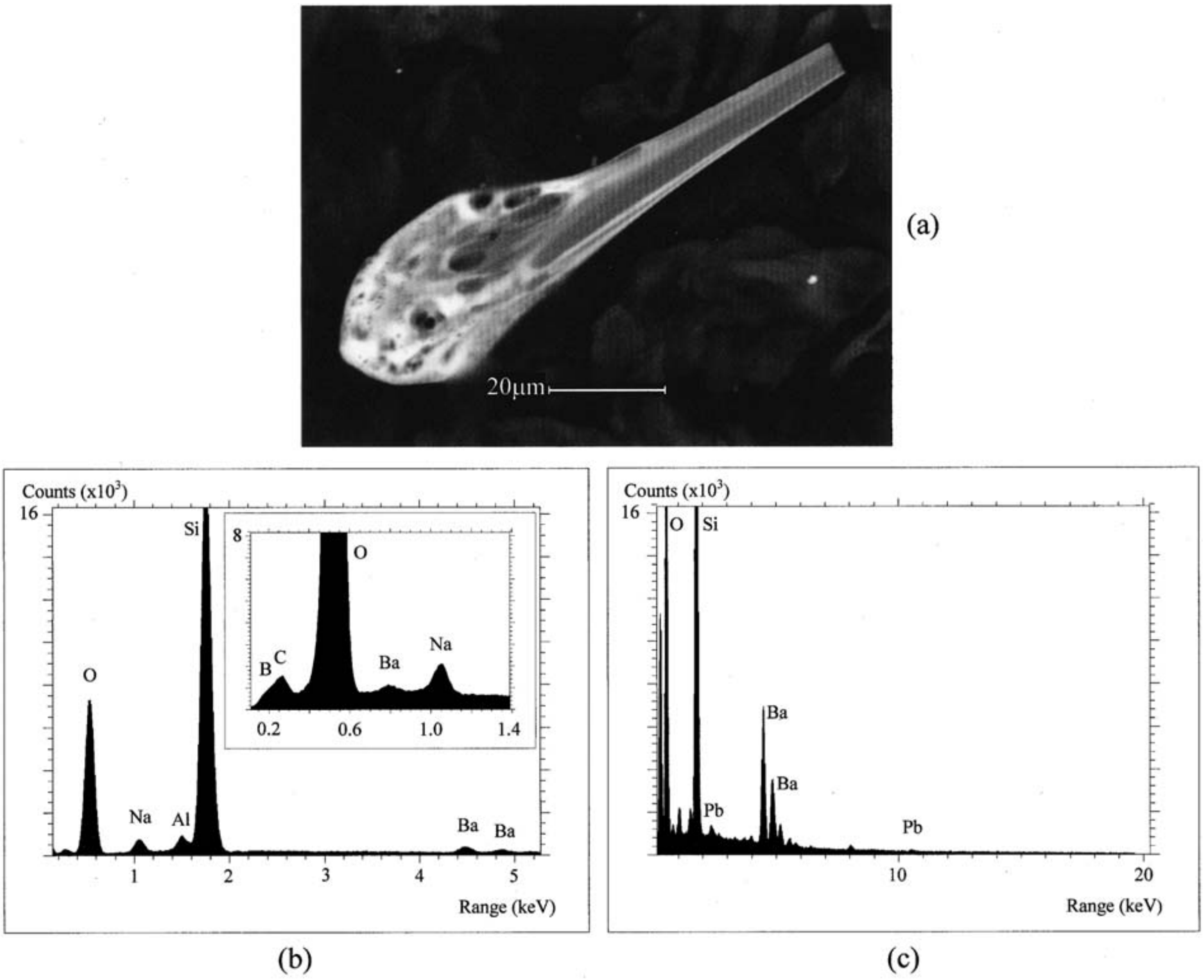


FIG. 19—(a) *SEM BSE image of a GSR particle recovered from the hand of a shooter.* (b) *SEM-EDX spectra from the dull region at accelerating voltages 25 and 7 kV (insert).* (c) *SEM-EDX spectrum from the bright region at accelerating voltage 25 kV.*

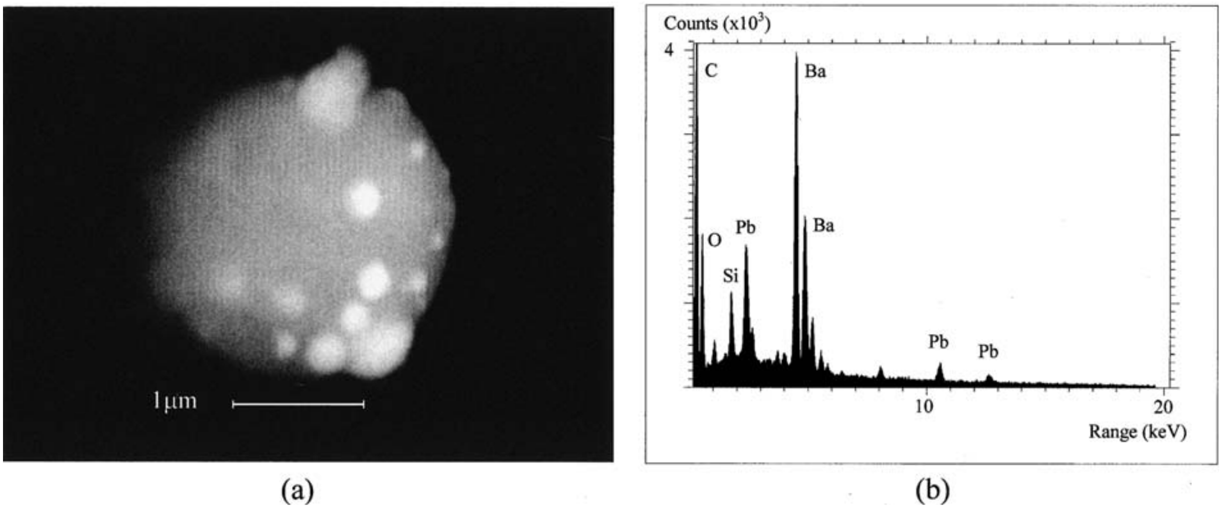


FIG. 20—(a) *SEM BSE image of a GSR particle recovered from the hand of a shooter.* (b) *SEM-EDX spectrum from the dull region at accelerating voltage 25 kV.*

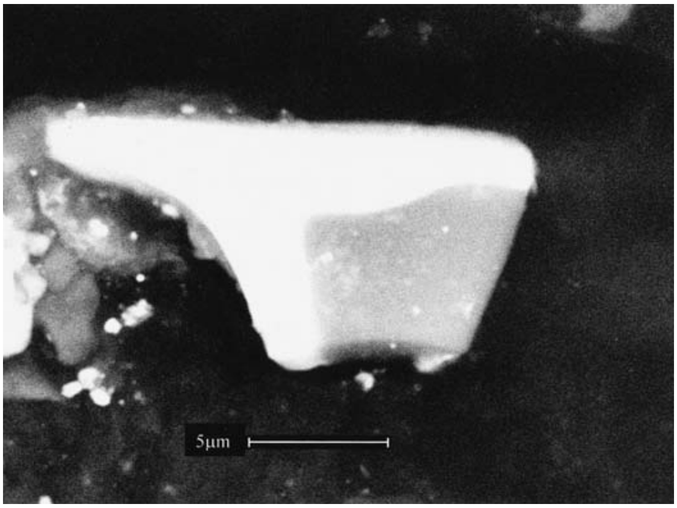


FIG. 21—*SEM BSE image of a glass-containing GSR particle recovered from a close range gunshot wound.*

TABLE 1—*SEM-EDX analysis of GSR particles recovered from fired cartridge cases.*

Sample	Lead and Barium on Borosilicate Glass	Sample	Lead and Barium on Borosilicate Glass
0.22 Long Rifle		**0.22 Long Rifle cont.**	
Browning High Velocity	✓	Winchester Dynapoint	✓
CCI Mini Mag	✓	Winchester Laser	✓
CCI Stinger	✓	Winchester Long Z	✓
Federal American Eagle	✓	Winchester Power Point	✓
Federal Hi Power	✓	Winchester Rabbit Ammo	✓
Federal Lightning	✓	Winchester Subsonic	✓
Federal Spitfire	X*	Winchester Super Speed	✓
Fiocchi Ultrasonic	X†	Winchester Super X	✓
Fiocchi Expansive	X†	**0.22 Magnum**	
Lapua Pistol	X†	CCI Maxi Mag	✓
PMC Zapper	X‡	Federal Magnum	X*
Remington Hi Velocity	X§	Winchester Magnum	✓
RWS High Velocity	✓‖	Winchester Power Point Magnum	✓
Stirling Hi Impact	X*	**Ramset Industrial**	
Winchester Bushman	✓	Ramset Power Load	✓

* Lead, barium, and antimony residues fused to borosilicate glass.

† Lead, barium, and antimony residues only.

‡ *Variable batches:* lead and barium residues fused to soda-lime glass, also containing magnesium, aluminum, and potassium; and lead and barium residues fused to borosilicate glass.

§ *Variable batches:* lead residues fused to soda-lime glass, also containing magnesium; and lead, barium, and antimony residues fused to soda-lime glass, also containing magnesium.

‖ *Mixture of particles:* Lead and barium residues fused to borosilicate glass, also containing potassium, titanium, and zinc; and lead and barium residues fused to soda-lime glass, also containing magnesium, aluminum, and potassium.

NOTE: A previous study (15) found that 0.22 Fiocchi ammunition produced lead and barium residue only.

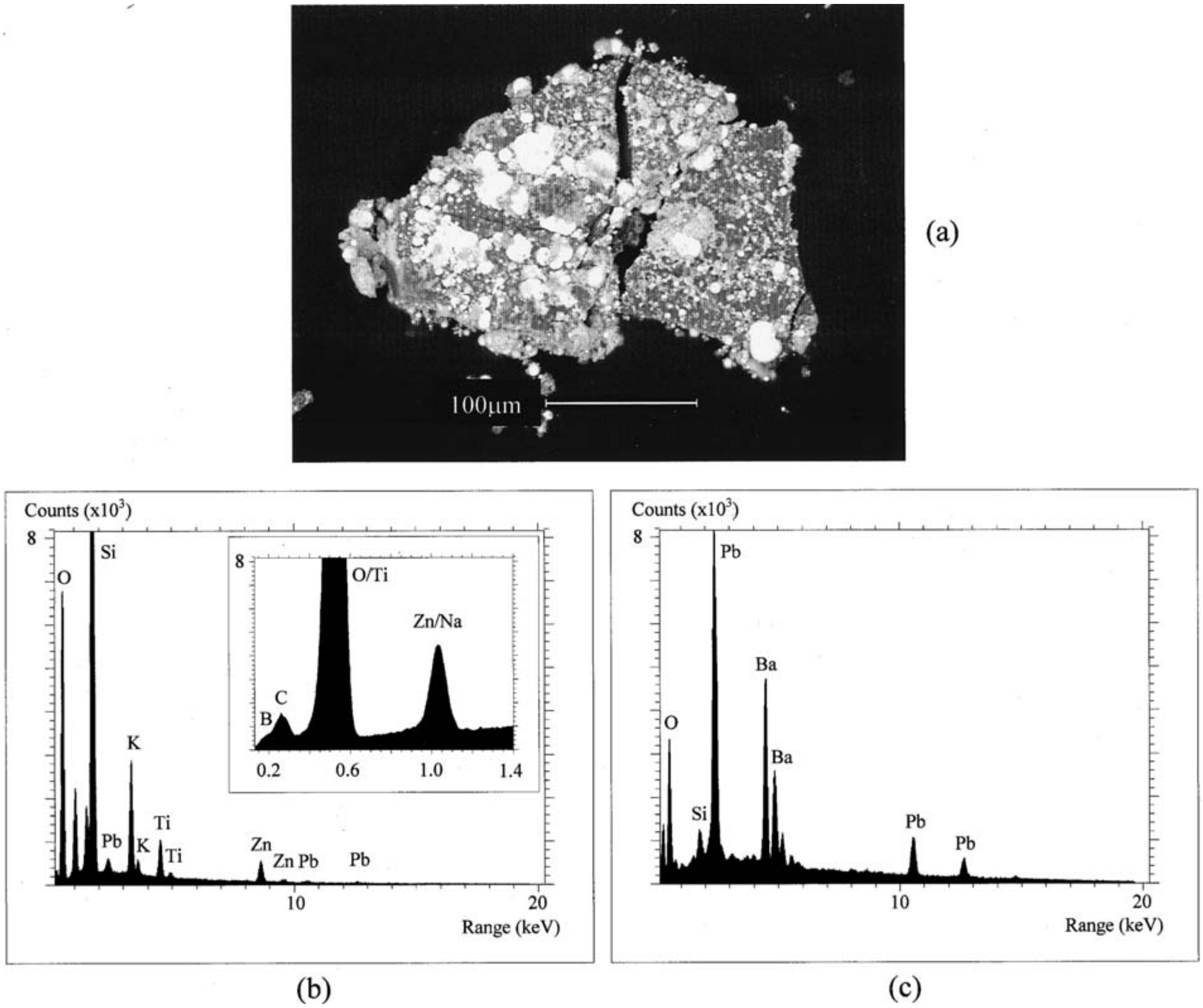


FIG. 22—(a) *SEM BSE image of a particle recovered from a fired RWS "High Velocity" cartridge case.* (b) *SEM-EDX spectra from the dull region at accelerating voltages 25 and 7 kV (insert).* (c) *SEM-EDX spectrum from the bright region at accelerating voltage 25 kV.*

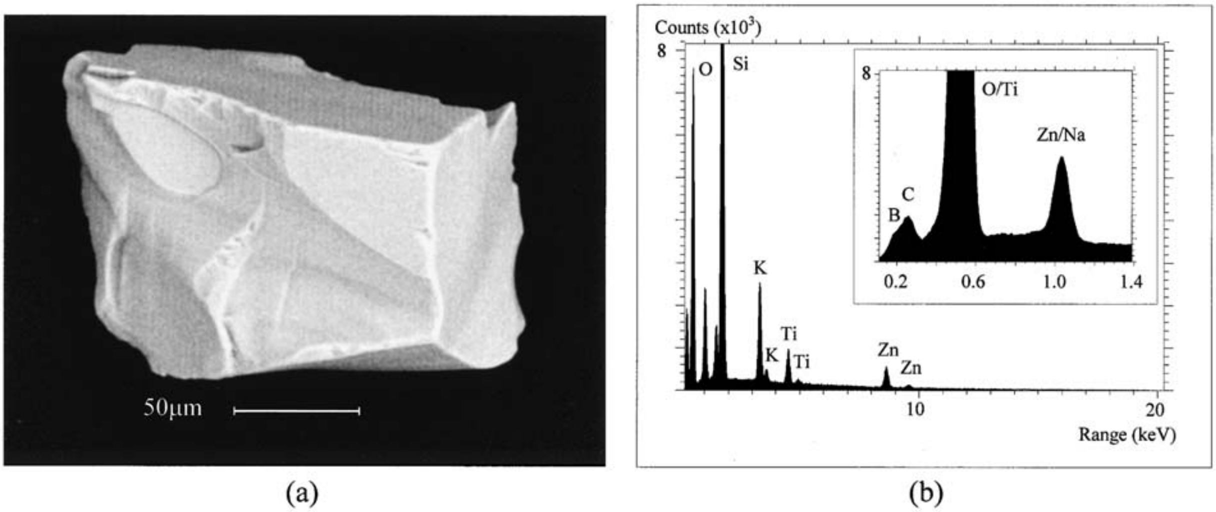


FIG. 23—(a) *SEM BSE image of glass from an unfired RWS "High Velocity" cartridge case (carbon coated).* (b) *SEM-EDX spectra at accelerating voltages 25 and 7 kV (insert).*

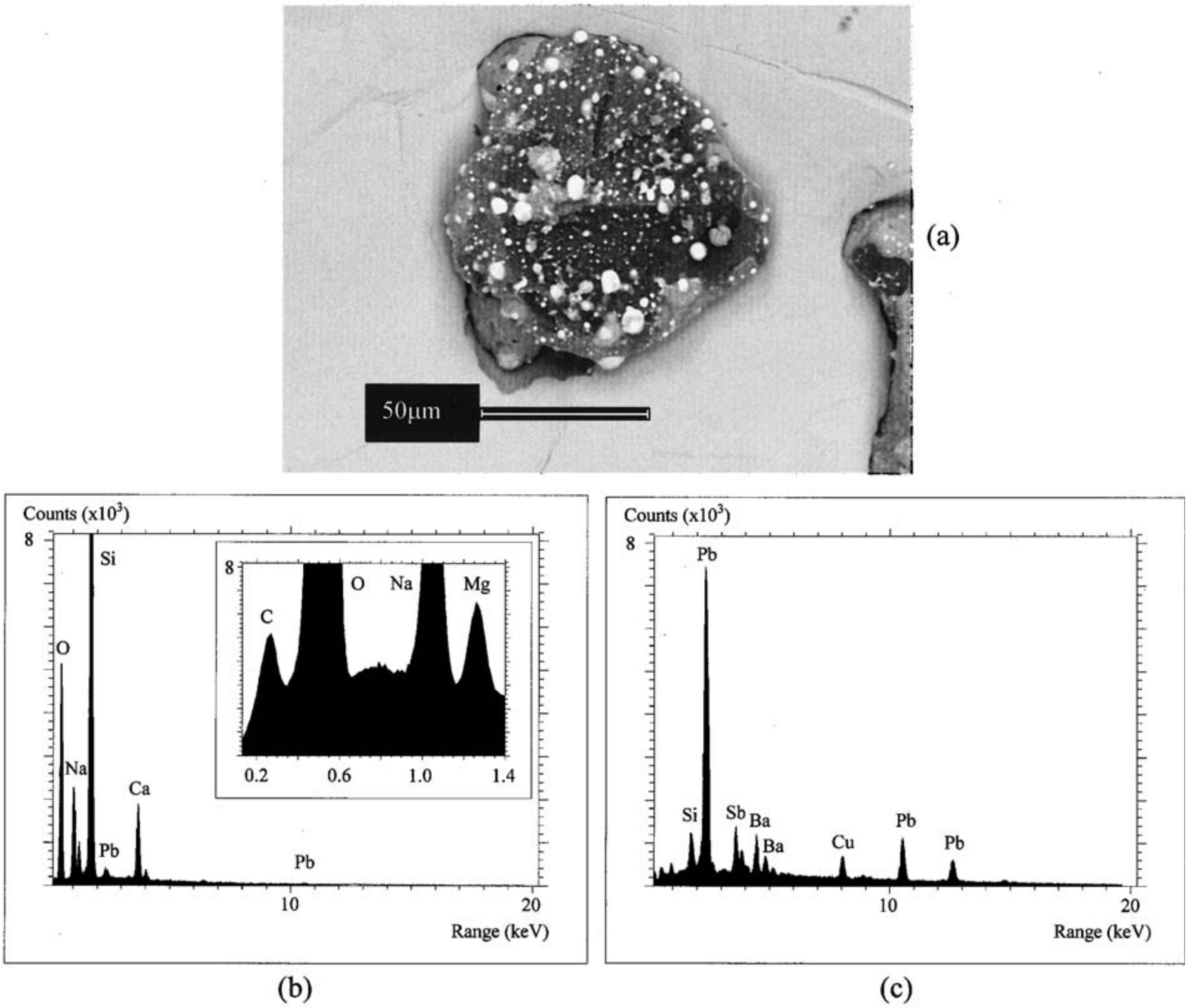


FIG. 24—(a) *SEM BSE image of a particle recovered from a fired Remington "Hi Velocity" cartridge case.* (b) *SEM-EDX spectra from the dull region at accelerating voltages 25 and 7 kV (insert).* (c) *SEM-EDX spectrum from the bright region at accelerating voltage 25 kV.*

per" and ground borosilicate glass was recovered from another. Remington "Hi Velocity" was the only ammunition that produced GSR particles comprising lead, barium, and antimony residues fused to soda-lime glass (Fig. 24). Another batch of Remington "Hi Velocity" was the only ammunition that produced GSR particles comprising lead residues fused to soda-lime glass. Obviously manufacturers may change the composition of their primers between batches. This should be considered in the interpretation of casework results.

The Ramset power tool cartridges with Winchester head stamps produced particles indistinguishable from those produced by Winchester 0.22 caliber ammunition.

Conclusion

This article describes GSR particles with exposed glass surfaces, which occur in the discharge residue from a variety of 0.22 caliber ammunition brands and may be detected on samples taken from hands and close range gunshot wounds. In the absence of a major survey, it is not possible to completely rule out the adventitious production of particles with similar composition and morphology to those described in this paper. However, it appears likely that such particles are highly characteristic of firearm discharge. This is of particular relevance to the GSR from 0.22 caliber ammunition in which antimony is not present.

SEM-EDX using a thin polymeric window has been demonstrated as a suitable technique for the detection and subsequent analysis of glass-containing GSR particles where glass surfaces are exposed. The SEM-EDX results indicate that the gross composition of regions of the glass may remain substantially unaltered during firing. A survey of ammunition types indicated that borosilicate glass and then soda-lime glass are the most commonly used frictionators in 0.22 caliber ammunition, with some sub-classification of these glasses possible. The survey also confirmed that 0.22 caliber ammunition may contain lead, lead and barium or lead, barium, and antimony-type primers. Therefore, this technique provides discrimination between some 0.22 caliber ammunition types based upon the gross elemental composition of the glass and the fused primer-derived residue.

TOF-SIMS analysis of the representative particle extracted from a fired cartridge case exemplifies the strengths TOF-SIMS offers as a complementary technique to SEM-EDX. In characterization of glass-containing GSR particles, the capability for depth profiling, elemental mapping and simple, and reliable detection of boron are important features. TOF-SIMS also has the ability to remove extraneous surface debris by etching. In addition, TOF-SIMS can be used to measure trace element profiles. This may prove to be a useful tool for comparative analysis of ammunition. An investigation of the potential applications for profiling by TOF-SIMS is continuing.

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