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Distribution of Lead and Barium in Gunshot Residue Particles Derived from 0.22 Caliber Rimfire Ammunition

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ABSTRACT: 0.22 caliber rimfire ammunition is commonly encountered in firearms incidents in Australia. This paper reports on work which has confirmed the nonhomogeneous nature of gunshot residue (GSR) particles and that the lead and barium distribution within particles varies significantly with the particle size and structure. The outcome has been an improved understanding of how the particle formation influences the ability to determine the origin of GSR derived specifically from 0.22 caliber rim fire ammunition.

KEYWORDS: forensic science, gunshot residue, scanning electron microscopy, 0.22 caliber ammunition

The composition of gunshot residues represents the products of primer and propellant combustion as well as contribution from the cartridge components and firearm. The main sources of GSR ejected from the breech are particles originating from the primer and bullet, with few partially burnt propellant particles (1).

The morphology of both bullet- and primer-derived particles is consistent with the theory of rapid cooling from extreme temperatures (1500 to 3600°C) and pressures (1400 to 40 000 psi) (2,3). It is currently accepted that GSR particles possess a characteristic spheroidal shape. This is also highlighted in ASTM E 1588: "Morphologically, the majority of GSR consist of spheroidal particles between 0.5 μm and 5.0 μm in diameter" (4). Furthermore, the established view is that GSR particles are condensates both in terms of their surface morphology (2,5) as well as their interiors (3). Basu (3) further states that when combining this morphology with the elemental composition, GSR particles are unique.

It is recognized that unique identification of GSR based on composition requires the detection of the three elements, lead, barium, and antimony, in individual particles. 0.22 caliber rim fire ammunition is commonly encountered in firearms incidents in Australia, and it is well known that many primers used in this type of ammunition do not contain antimony, making unique identification of the GSR particles difficult. However, a lead-barium composition combined with the characteristic morphology would provide more reliable identification of 0.22 derived GSR.

Earlier work in our laboratory (6) had shown that the proportion of particles produced by 0.22 caliber ammunition that contain both lead and barium can be quite small and that the barium-containing particles are often the larger ones (>5 μm). Since the larger particles are the first to be lost, this will further limit the ability to identify GSR from 0.22 ammunition.

Similar to work conducted by Matricardy and Kilty (7), the aim of this work was to determine whether a correlation exists between particle size, morphology, and elemental composition specifically for 0.22 caliber ammunition gunshot residues. Such a relationship may prove to be useful in the case of 0.22 ammunition where primer formulations vary and may not produce particles with a unique GSR composition but a unique GSR morphology, and may subsequently enhance confidence in interpreting results obtained in casework involving such ammunition.

Materials and Methods

Firing of Weapons and Collection of Gunshot Residue

The firearm used for all investigations was a 0.22 LR 4-in. barrel Smith and Wesson Model 18/3 revolver. Winchester Super Speed 0.22 LR (copper-plated projectile) ammunition was used for Samples 1 to 4 and Fiocchi 0.22 LR ammunition was used for Sample 5.

Samples 1 and 2—Samples were collected by tape-lifting both hands of two subjects 20 min after each had fired three shots using the same Winchester rimfire ammunition. The samples were analyzed by scanning electron microscopy (SEM), equipped with an energy dispersive X-ray detector for particles containing lead and barium, and then re-examined for particles containing lead only.

Sample 3—Further samples were obtained by tape-lifting the hands of a subject after six rounds of Winchester 0.22 rimfire ammunition had been fired. The samples were examined manually by SEM, and particles located randomly in the size range less than 3 μm and greater than 5 μm were analyzed.

Samples 4 and 5—In order to determine whether there is a trend between particle morphology and composition, and to further evaluate the trend between particle size and composition, two experiments were performed. The hands of a subject were sampled after multiple rounds of Winchester (12 shots, Sample 4) and Fiocchi (18 shots, Sample 5) brand 0.22 caliber ammunition had been fired from a revolver. The results obtained from these two experiments

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were also compared to GSR particles analyzed in an actual case involving a suicide.

After the experiment using Winchester ammunition was completed, the firearm was "purged" by firing six equilibrating shots with the Fiocchi ammunition. As Winchester ammunition contains silicon, and particles containing silicon were not detected in the experiment using Fiocchi ammunition, it was concluded that cross-contamination from one experiment to the next had not occurred.

Scanning Electron Microscopy

Instrumental Operating Parameters—A Camscan Series 4 Scanning Electron Microscope (Camscan Electron Optics Ltd, Cambridge, UK) incorporating a Camscan Fasttrac stage with automated particle identification, Camscan Editor energy dispersive X-ray analytical software, an EDAX EDAM II energy dispersive X-ray detector (EDAX International, New Jersey), and a Camscan Robinson backscatter detector was employed. The accelerating voltage was set at 25 k V, and a stage tilt of 10° and working distance of 35 mm was used. The automated particle search was conducted at a magnification of 1900×.

Sample Collection—Sampling from the hands of all subjects was performed on 12 mm diameter pin type aluminum SEM mounts containing an adhesive tab (ProSciTech, Queensland, Australia). All samples were coated with a thin layer of conductive carbon prior to analysis.

Results and Discussion

Lead-Barium Distribution in 0.22 Caliber Primer Residues: Particle Size–Composition Relationship

For Samples 1 and 2, a large number of GSR-related particles were found (~800 particles analyzed for Sample 1 and ~700 particles analyzed for sample 2). However, of these particles only a small number were found to contain both lead and barium, with the majority of the particles classified as small (<5 μm) lead spheres (770 lead particles from Sample 1 and 660 lead particles for Sample 2). Upon analysis of the projectile, it was concluded that the large number of lead particles were due mainly to bullet-derived residues. Figures 1 and 2 illustrate the particle-size distribution of particles found to contain both lead and barium.

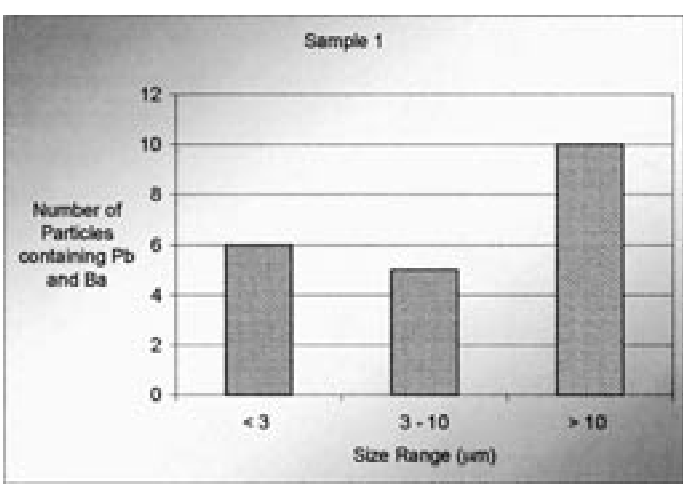

FIG. 1—*Size distribution of lead-barium particles—Sample 1. Due to the small number of particles in the 3 to 10 μm size range, the distribution was not broken down further.*

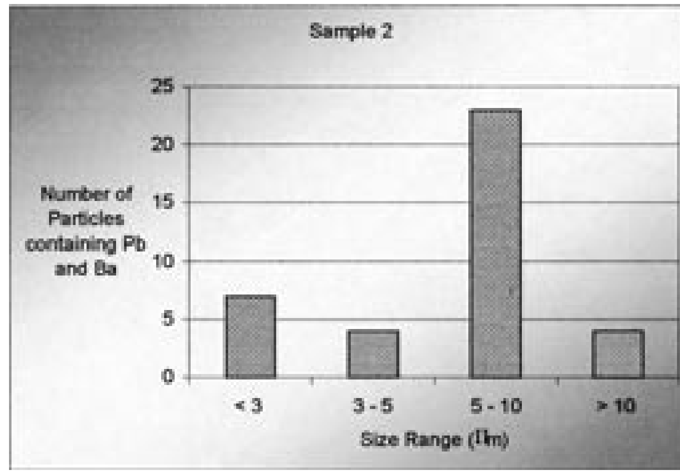

FIG. 2—*Size distribution of lead-barium particles—Sample 2.*

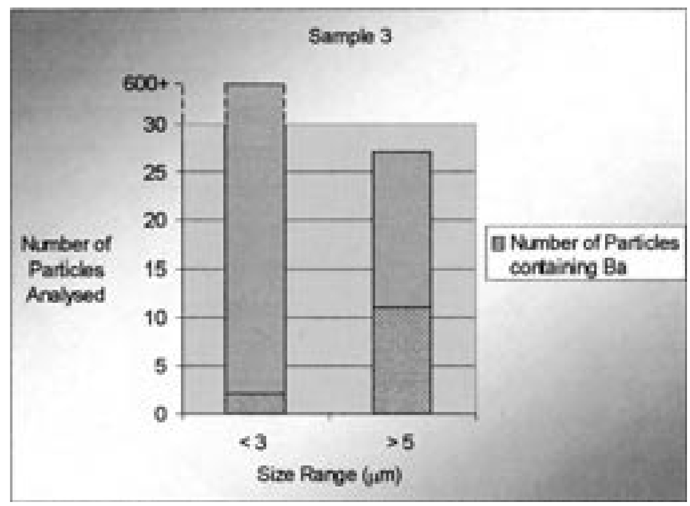

FIG. 3—*Presence of Ba relative to particle size. The large number of particles <3 μm were attributed to bullet-derived gunshot residues.*

These results indicate that only a small fraction of the particles produced when 0.22 rimfire ammunition is fired from a revolver can be expected to contain both lead and barium. Only 3 and 6% of particles analyzed for Samples 1 and 2, respectively, contained lead and barium. Furthermore, barium tends to be associated with the larger particles (>5 μm) while the smaller particles (<3 μm) tend to be composed of lead with no barium evident, as shown in Fig. 3. This general trend has been observed in casework.

As can be seen from Fig. 3, it is evident that the barium-containing particles tend to be large. This trend was further evaluated by analyzing hand swabs of two subjects after firing multiple rounds of Winchester (Fig. 4) and Fiocchi (Fig. 5) brand 0.22 caliber ammunition.

From the data illustrated in Fig. 4, 74% of lead particles are in the 0 to 15 μm size range, 91% of lead/barium particles are in the 6 to 30 μm size range, and, finally, 58% of lead/barium/silicon particles are in the 31 to 60 μm size range. It should also be noted that a large number of particles of diameter <5 μm contained antimony and copper and have not been illustrated in Fig. 4. The copper is attributed to the copper plating of the projectile, and it would appear

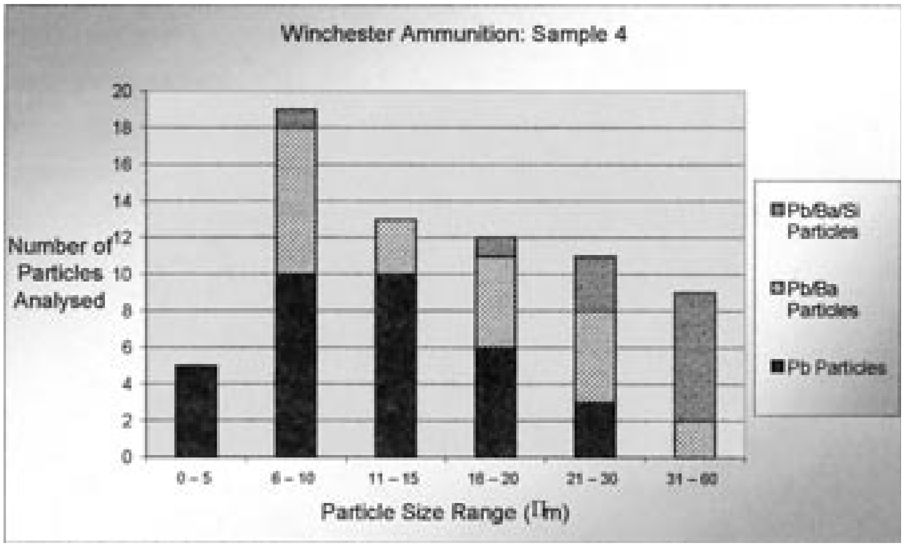

FIG. 4—*Variation of elemental composition relative to particle size—Winchester ammunition.*

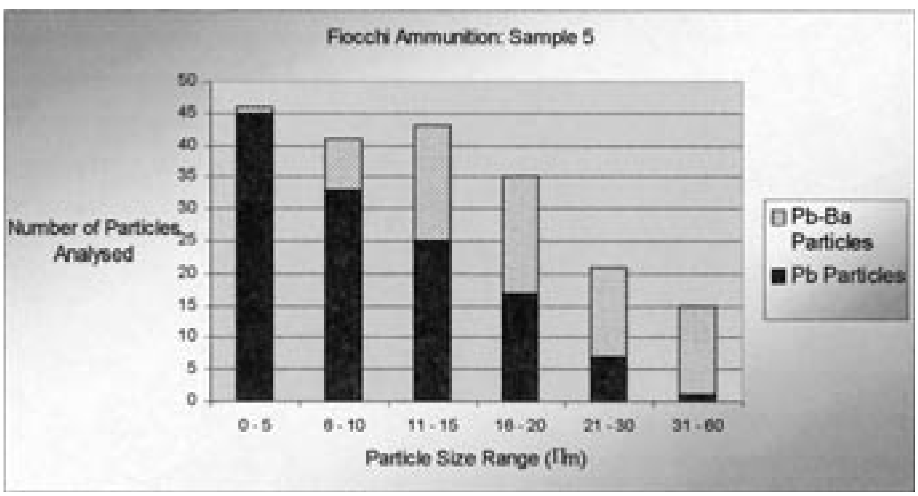

FIG. 5—*Variation of elemental composition relative to particle size—Fiocchi ammunition.*

that the antimony is present as a hardener in the projectile. These results therefore suggest that particles of this size (<5 μm) and composition (lead, copper, and antimony) tend to be bullet derived. This was confirmed upon analysis of the projectile.

From the data illustrated in Fig. 5, 61% of lead particles are in the <10 μm size range. Note that as the projectile was not copper coated and did not contain antimony, bullet-derived lead particles could not be distinguished from primer-derived particles and are thus included in the <10 μm size range. As a consequence, a large number of particles were analyzed and counted in this size range. In the >10 μm size range, the relationship between size and composition is further emphasized as 88% of the particles contained lead and barium.

Lead-Barium Distribution in 0.22 Caliber Primer Residues: Particle Morphology-Composition Relationship

GSR particles obtained from the Winchester (Sample 4) and Fiocchi (Sample 5) ammunition were also used to examine the relationship between morphology and composition. The particles selected for this investigation showed characteristic GSR morphology consistent with condensation from high temperature and pressure (i.e., spherical particles with a globular appearance).

A number of general morphology-composition relationships were evident from the observations recorded. Two clear features were: (i) a rough-textured appearance and (ii) a smooth globular appearance. These texture differences were also evident from the difference in image contrast. In general, lead dominated in the rough-textured areas, and the smooth globular areas had high levels of barium and/or silicon.

From the particles illustrated it can be seen that the larger (>10 μm) spherical GSR particles that contained lead-barium-silicon (Winchester, Fig. 6) and lead-barium (Fiocchi, Fig. 7) exhibited a complex surface morphology. The results indicate that these particles have an irregular and discontinuous distribution of elements across the surface. Particle regions that gave high signals for barium also had a glazed globular appearance to them, whereas particles rich in lead were granular and "rough" textured.

Crater and cavity formation is a general characteristic of larger GSR particles (>10 μm). By focusing the electron beam into these

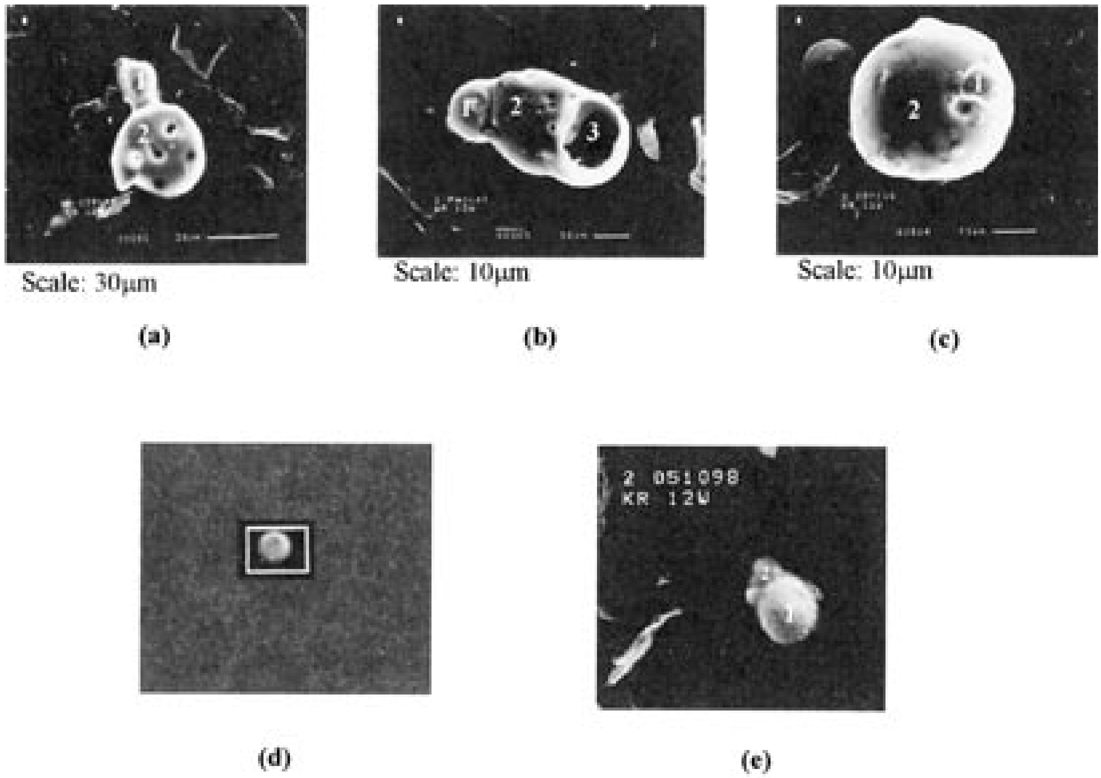

FIG. 6—*GSR particles derived from 0.22 Winchester ammunition: (a) Particle 1: Region 1—Rough texture; lead, barium, trace silicon; Region 2—Smooth globular appearance; barium, silicon, trace lead. Analysis of cavities indicated silicon composition.*
(b) Particle 2: Region 1—Lead only.
Region 2—Barium and silicon. Analysis of cavities revealed a silicon rich core.
Region 3—Popped cavity; barium-rich interior surface.
(c) Particle 3: Region 1—Lead nodule.
Region 2—barium, silicon and lead.
(d) Particle 4: 3 μm spherical bullet-derived GSR particle composed of lead and copper.
(e) Particle 5: Region 1: Rough textured spheroid; lead rich.
Region 2: Protruding skirt; barium rich.

areas, analysis of the core of the particle was possible. Analysis of cavities tended to reveal increased levels of barium and silicon. For example, when the electron beam was focused into the craters (Figs. 6*a* and 6*b*), the silicon counts increased, indicating that the core is mainly silicon. Analysis of cavities, as in Winchester Particle 2 (Fig. 6*b,* Region 3), exposed the interior surface of the particle and indicated that the internal surface is mainly barium. It therefore appears that lead tends to form a layer around a barium (Fiocchi) or barium-silicon core (Winchester), an observation consistent with literature (3).

An interesting result was observed for Fiocchi particle 2 (Fig. 7*b*). From the size-composition trend, it would have been expected that the 4 μm spheroid would have been mainly lead, yet barium was also evident. The attached 10 μm spheroid would have been expected to contain barium, whereas it was lead only. Close examination of this particle, however, revealed that the 4 μm spheroid had a smooth globular appearance and the larger spheroid had a rough-textured appearance. These observations therefore agree with the morphology-composition relationship described above.

The results obtained for the non-antimony containing 0.22 caliber primers studied here show a clear size-composition and morphology-composition relationship. These correlations contribute significantly to the interpretation of analytical results. The observed nonhomogeneous distribution of elements and significant composition variation as a function of particle size appears to contradict results obtained in a recent study by Lebiedzik and Johnson (8). However, the ammunition used in their study was not limited to 0.22 caliber ammunition and in addition contained antimony.

The complex morphology and composition observed here can possibly be explained by referring to the solidification temperatures of the elements lead (327°C), barium (725°C), and silicon (1410°C). The respective temperatures would suggest that silicon would solidify first, providing a nucleus for condensation of barium, with a final deposition of lead forming the outer layer around the particle (assuming that the elements are deposited in the elemental form). We have observed that the presence of lead can be seen as individual nodules surface captured onto particles (Fig. 6*c*), or as an entire membrane of surface nodules (Figs. 6*e* and 7*d*). Thus it is possible that particles showing an X-ray spectrum of lead only may well have an inner core of barium.

Similar results have been observed in casework. Comparison of the Fiocchi- and Winchester-derived GSR particles with those obtained from the hands of a suicide victim revealed that the morphology observed for GSR particles from the test-fired ammunition is consistent with actual case samples. Furthermore, as was evident from the suicide case GSR particles (Fig. 8), differences in the image contrast of the particle indicated intricate differences in the particle composition.

Table 1 is a brief summary of the characteristic features observed for the 0.22 caliber primer residue particles analyzed.

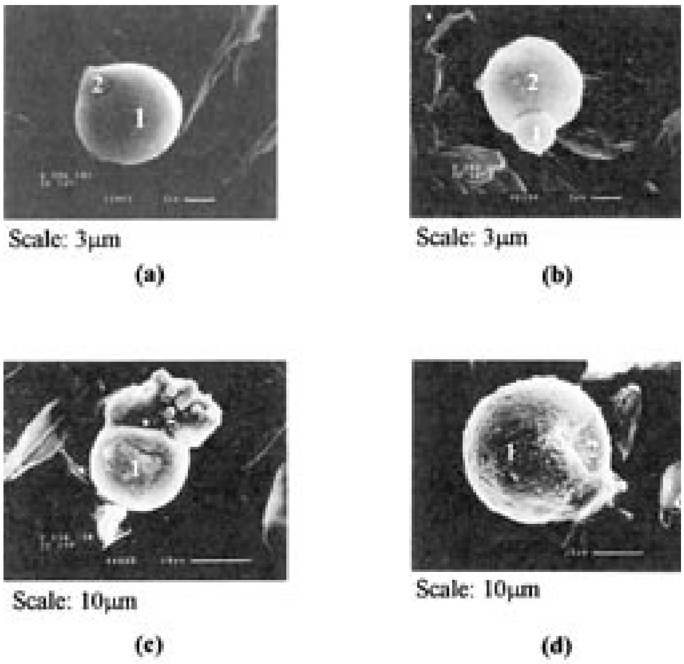

FIG. 7—*GSR Particles derived from 0.22 Fiocchi ammunition. (a) Particle 1: Region 1—Rough textured surface; lead.*
Region 2—Protruding globular region; lead and barium.
(b) Particle 2: Region 1—Smooth ~4 µm spheroid; lead and barium.
Region 2—Rough-textured 10 µm spheroid; lead only.
(c) Particle 3: Region 1—Rough-textured 20 µm spheroid; lead.
Region 2—Protruding "comb" region; lead and barium.
Lead spheroids surface captured on Region 2.
(d) Particle 4: Region 1—Lead with trace barium.
Region 2—Cavity; barium rich.

TABLE 1—*Characteristics of 0.22 caliber primer residues.*

GSR Particle Appearance	Composition
Rough textured	Lead
Smooth-globular	Barium (Fiocchi) Barium and/or silicon (Winchester)
Craters	Barium (Fiocchi) Silicon and trace barium (Winchester)
Craters exposing interior surface	Barium
Surfaces-captured nodules	Lead

Conclusion

Despite the fact that most 0.22 caliber ammunition does not produce three components (lead, barium, antimony) GSR, the fact that they have a distinct composition and morphology consistent with high temperature and pressure condensation should increase reliability in interpreting such results in forensic casework. The characteristic morphology combined with the trends in composition and size could be important factors in confirming a GSR origin for the particles. Furthermore, extra information can be gained by analyzing different regions of a suspected GSR particle. It is also possible that the presence of barium may be missed in some particles where it is the core covered by a layer of lead.

However, the proportion of particles containing both lead and barium in relation to the total number of GSR particles produced is small. Furthermore, it is the larger particles that show the characteristic morphology and composition relationship. This is a limiting factor as the larger GSR particles (>10 µm) tend to drop off a "shooters" hands rather rapidly, further increasing the complexity of results obtained from 0.22 caliber ammunition.

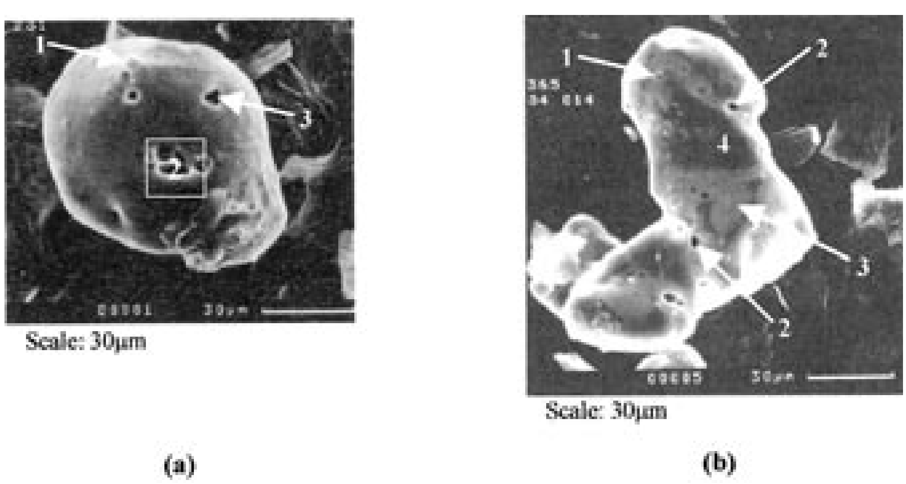

FIG. 8—*Casework GSR Particles. (a) Particle 1: Exhibited the same globular smooth textured appearance with cavities observed previously.*
Region 1—Surface captured ~4 mm nodule; lead only.
Region 2—Surface containing cavities; barium and silicon with trace lead.
Region 3—Spot analysis on cavity; barium and silicon.
(b) Particle 2: Irregular-shaped particle with composition and surface morphology consistent with observed trends.
Region 1: Surface captured nodule; lead and trace barium.
Region 2: Cavities; silicon with trace lead. It was found that the bright-contrast regions (Region 3) were barium and silicon, whereas dark-contrast regions (Region 4) also contained lead.

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