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TECHNICAL NOTE

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Evaluation of Shooting Distance by AFM and FTIR/ATR Analysis of GSR

ABSTRACT: The techniques of atomic force microscopy (AFM) and Fourier transform infrared attenuated total reflectance (FTIR/ATR) spectroscopy are applied to the analysis of gun-shot residue (GSR) to test their ability to determine shooting distance and discrimination of the powder manufacturers. AFM is a nondestructive technique that is capable of characterizing the shapes and size distributions of GSR particles with resolution down to less than a nanometer. This may be useful for estimation of the shooting distance. Our AFM images of GSR show that the size distribution of the particles is inversely proportional to the shooting distance. Discrimination of powder manufacturers is tested by FTIR/ATR investigation of GSR. Identifying the specific compounds in the GSR by FTIR/ATR was not possible because it is a mixture of the debris of several compounds that compose the residue. However, it is shown that the GSR from different cartridges has characteristic FTIR/ATR bands that may be useful in differentiating the powder manufacturers. It appears promising that the development of AFM and FTIR/ATR databases for various powder manufacturers may be useful in analysis and identification of GSR.

KEYWORDS: forensic science, GSR, AFM, shooting distance, FTIR/ATR

The detection and analysis of gun-shot residue (GSR) is essential for approximating the firing distance (1–6) and verifying whether a suspect has fired a gun (4,7,8). The most commonly used technique in characterization of GSR is currently the technique of scanning electron microscopy (SEM) with the attachment, X-ray energy dispersive spectrometry (EDS) (7–9). The sample must be conductive for SEM analysis. SEM samples are usually coated with a conductive layer, such as carbon. This may mask some of the features of the sample surface. The sample is thus contaminated and cannot be used for analysis by other methods (10). The estimation of shooting distance, when combined with other evidence, is important in reconstructing shooting events. The appearance of the bullet entrance hole and the GSR patterns around the hole are usually used to estimate the firing distance (1–6). A variety of chemical and physical methods have been applied to obtain the GSR patterns (4–6). The Griess test and a series of modified and improved Griess tests are used as a color test for nitrites and a procedure for estimation of muzzle to target distance (1–6). Chemical analyses in investigation of firearm-related events have recently been reviewed by Zeichner (4) and Zeichner and Glattstein (6).

Herein, we report on the application of atomic force microscopy (AFM) and Fourier transform infrared attenuated total reflectance (FTIR/ATR) spectroscopy as possible new methods for estimation of the firing distance or muzzle-to-target shooting distance, and the manufacturers of the cartridge and its powder. The technique of AFM, which was developed by Binnig et al. (11) in 1986 has the potential for providing new information and methods of analysis of GSR. AFM can be applied to the investigation of various materials regardless of their conductivity. Unlike SEM which can only operate in vacuum, AFM is a nondestructive technique in which measurements can be made in either air, liquid, or controlled atmospheres. This allows the intact sample to be characterized by AFM without the need of any pretreatments, thereby allowing further sample analysis without any contamination from the AFM. Herein we report a novel application of AFM for approximating firing distances by studying the size distribution of the GSR. The distance that GSR particles travel from the barrel will depend on their size and shape or morphology.

FTIR spectrometry has been applied to various areas of forensic science (12–14). Traditional FTIR measurements require special sample preparation procedures. However, the ATR microscope, an accessory of FTIR, requires no sample preparation. Both transparent and nontransparent samples (14) can be investigated without any special preparation procedures. Sample areas as small as 1 mm^2 can be investigated with a resolution of <1 μm^2. These advantages are powerful and effective in obtaining vibrational spectra of GSR deposits. Analysis of lead-free primers (8) has mainly been conducted by analyzing the elements of GSR using EDS, an accessory of SEM. Herein, we apply FTIR/ATR spectra to characterize the GSR from different manufacturers of the cartridge and its powder.

Experimental

Ammunition, Shooting, and Sampling

A Remington model 552 rifle using 0.22 caliber long-rifle high-velocity cartridges were used in the experiments. The three cartridge manufacturers used were CCI, Winchester SuperX, and Remington (CCI Industries, Lewiston, ID; Remington Arms Co., Inc., Bridgeport, CT; and Winchester—Western Division, Olin New Haven, CT). Shots were fired at muzzle-to-target distances of 6 inches, 2 ft, and 20 ft. GSR was collected on 8.5 inch × 11 inch polyethylene and aluminum foil sheets that were affixed to a target board. The sheets were removed from the target board after shooting and stored in clean boxes for later analysis. The shooting was done outdoors on a calm, nonwindy day with the gun in a horizontal position and the target in a vertical position. The gun

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barrel was cleaned before commencing firing bullets from each of the three cartridge manufacturers using a clean white cloth swab. Plain lead round-nosed bullets were used for all of the experiments. Five shots were obtained at each of the four shooting distances.

Polyethylene was chosen as one of the supports for the GSR because it is transparent and smooth, allowing easy AFM visualization and analysis of the particles. Aluminum foil was chosen as one of the supports for the GSR because it is transparent in the infrared (IR) region, making it ideal for ATR analysis. Future investigations will include porous surfaces that are common in case work, such as cloth.

AFM

The size, morphology, and density of GSR particles were characterized by AFM using a Quesant Q-Scope™ 250 Nomad™ (Ambios Technology, Inc., Santa Cruz, CA). The tapping mode was used because of its high resolution capabilities. The scan resolution was set at 600 and the scan rate was set at 2 or 3 Hz according to the degree of roughness of the sample surface. The lower scan rate corresponds to a higher roughness. The stage allows samples as large as 20 cm × 20 cm in size and any area within this region can be scanned. The largest area selected for each scan was 40 μm × 40 μm. Circular areas with radius of 30 mm (28.3 mm^2 area) centered on the bullet entrance holes were investigated. Four bullet holes were investigated for each shooting distance.

Size Measurement

One of the advantages of AFM is that it is easy to make quantitative measurements of particle sizes. An image created by an AFM is stored in a computer as a three-dimensional array of numbers and can be displayed and analyzed in many formats. For a two-dimensional image, a single line or slice is made across this image. From the profile, the size of the GSR particles can be precisely measured by calculating the relative spacing between two points on the line. Figure 1 shows an example of particle size measurement. In Fig. 1*a*, the black line slicing through the two particles indicates where cross-sections of the image are being taken. Figure 1*b* shows a plot of the cross-sections of two particles. The distance between the neighboring arrows indicates the diameter of the particle. Approximately 500 particles were measured to obtain the size distributions at each different shooting distance.

FTIR/ATR

The ATR measurements of GSR were made on a Tensor 27 FTIR spectrometer with a Hyperion 1000 ATR microscope accessory, both of them are from Bruker Optics, Inc. (Billerica, MA). The ATR microscope measures the changes that occur in a totally internally reflected IR beam. Total reflection occurs when a sample is brought into direct contact with an optically dense crystal with a high refractive index. The IR beam is reflected from the optically dense crystal at a certain angle. When the angle of incidence of the beam from the crystal to the sample exceeds the crystal angle, total internal reflection takes place. The beam penetrates very slightly into the sample, producing an absorbance-like spectrum. GSR particles for FTIR analysis were chosen through a 20× ATR objective, which has a germanium crystal.

Results and Discussion

Morphology of GSR Particles

The GSR particles that have been investigated by SEM are generally spherical in shape (8), although other irregular shapes have been observed. Our measurements show that the GSR particles exhibit various shapes, although many of the particles are spherical. Figure 2 characterizes some representative AFM images of GSR with different shapes. These images are all from the GSR of the CCI cartridge at a shooting distance of 10 ft. Many different particle shapes are observed, including spherical, nonspherical, irregular, twins-like (Fig. 2*a*), heart-like (Fig. 2*b*), boomerang-like (Fig. 2*c*), rod-like (Fig. 2*d*), and cube/rectangular-like (Fig. 2*d*) GSR particles.

Direct observation of the size distribution of the GSR particles for different shooting distances is shown in Fig. 3. The shooting distances are 20 ft (Fig. 3*a*), 10 ft (Fig. 3*b*), 2 ft (Fig. 3*c*), and 0.5 ft (Fig. 3*d*). The images are taken for the CCI cartridge. By comparing the four images, we can directly observe the influence of shooting distance on the size and density of GSR particles. In (Fig. 3*a*), the GSR particles are sporadic and small. In (Fig. 3*d*), the GSR particles are much larger and denser. The images reveal that the average size of the deposited GSR particles becomes larger as the shooting distance is shortened. As this may only apply to certain particles with certain morphology, further testing is required to ascertain the generality of the role of shooting distance in the particle size distributions.

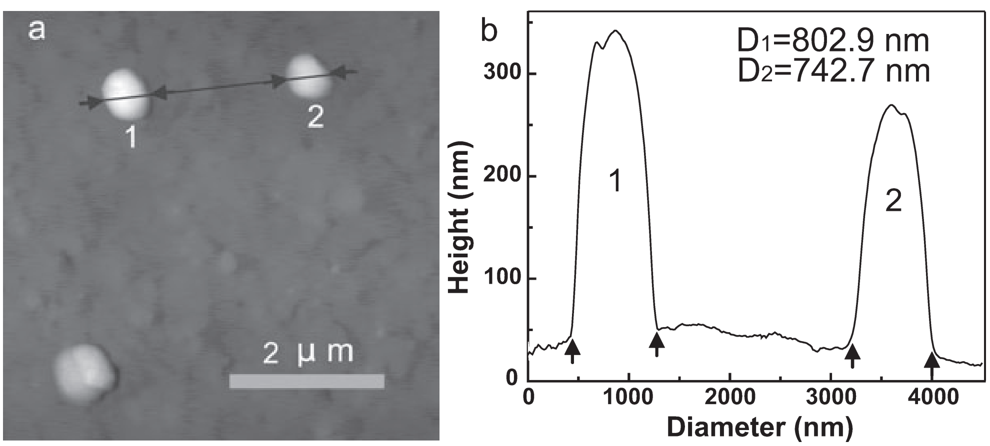

FIG. 1—*Demonstration of particle size measurement by AFM: top-view of the AFM image (a) and cross section of the image (b). The arrows indicate the measuring points.*

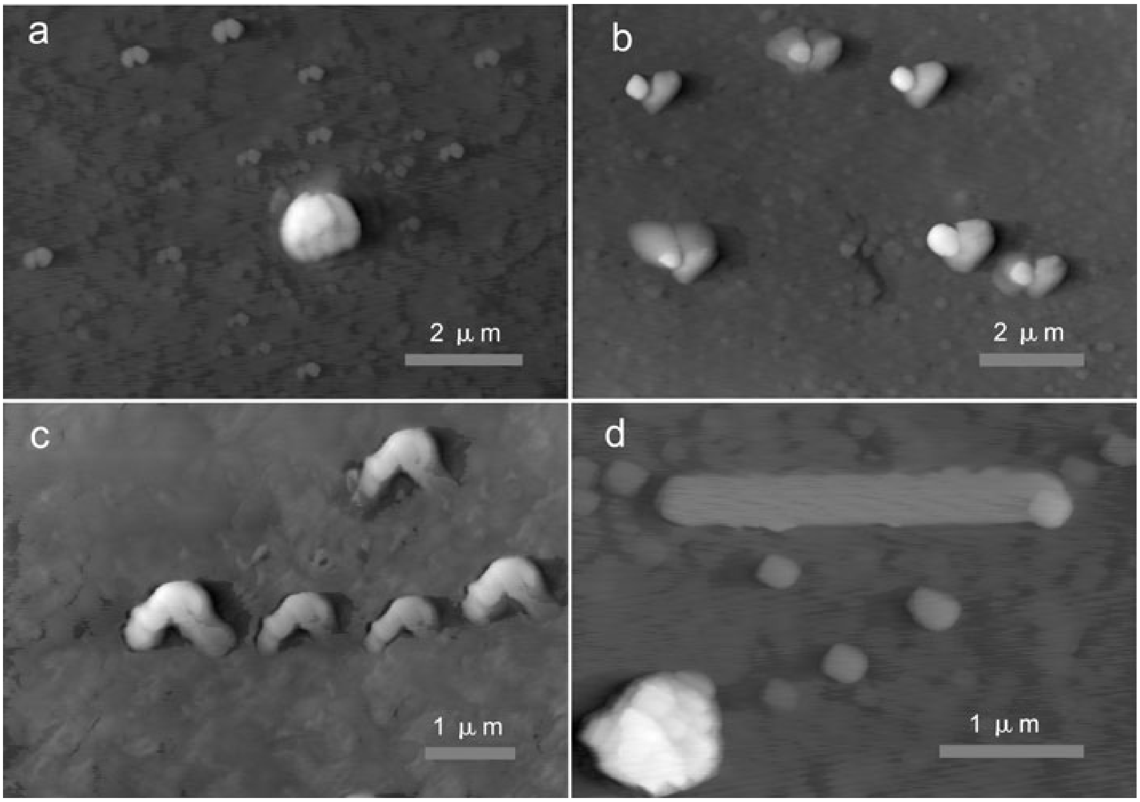

FIG. 2—*AFM images of GSR particles showing various particle shapes, twins-like (a), heart-like (b), boomerang-like (c), and rod and cube like (d). The bullet type is CCI and the shooting distance is 10 ft.*

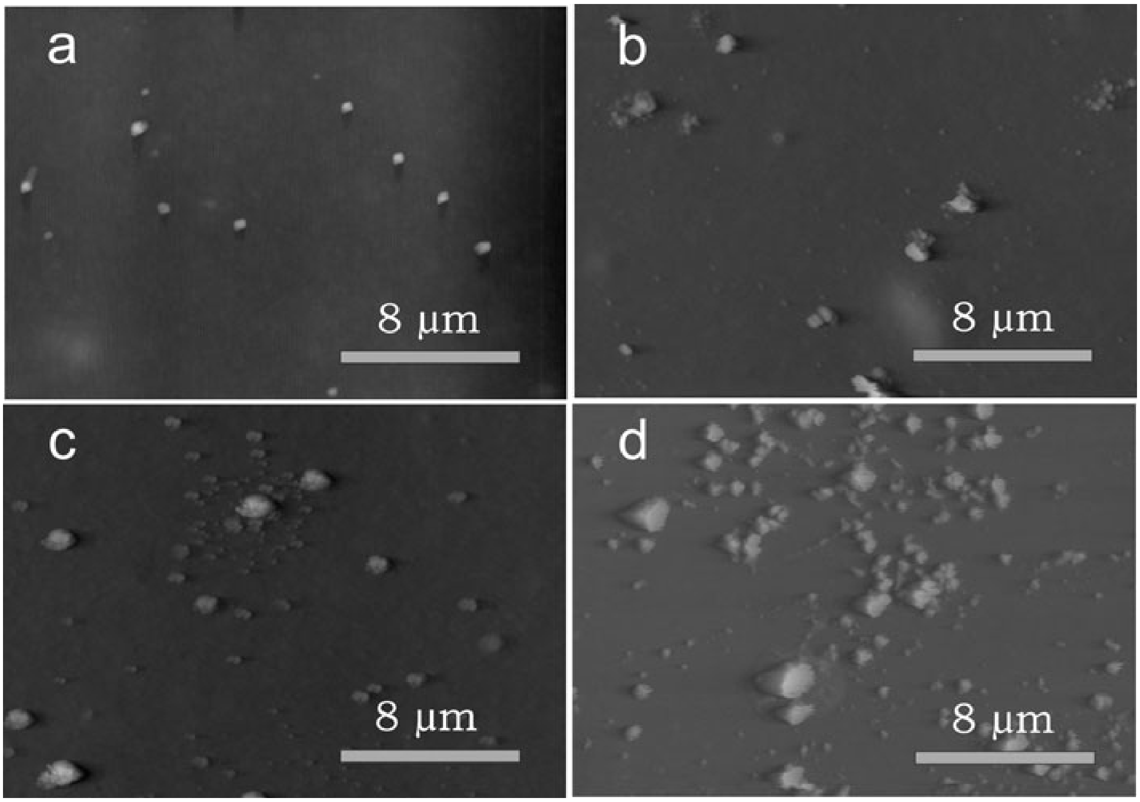

FIG. 3—*AFM images of GSR with different shooting distances. The bullet type is CCI. The shooting distances are 20 ft (a), 10 ft (b), 2 ft (c), and 6 inches (d).*

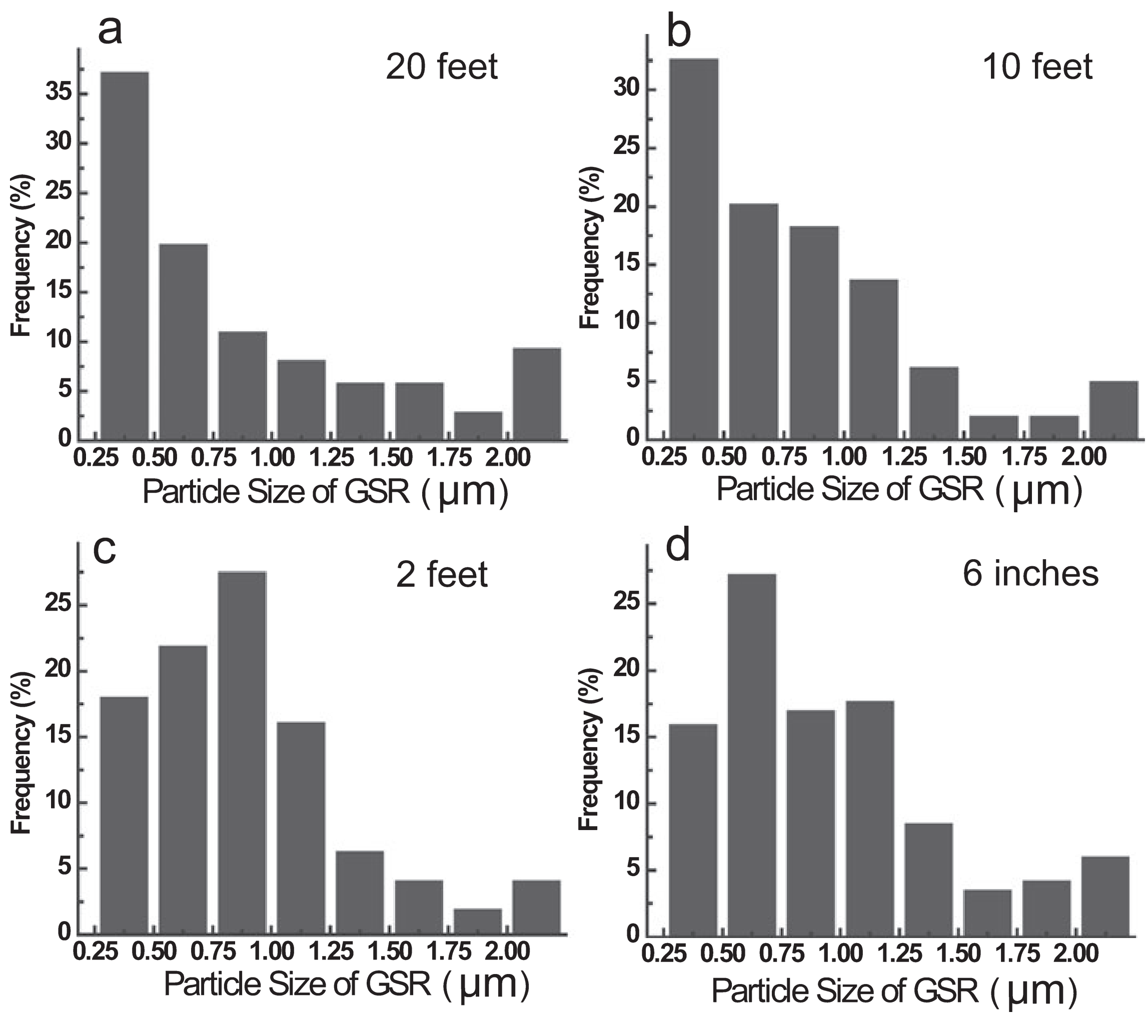

FIG. 4—*GSR particle size distribution of CCI cartridges with different shooting distances. The shooting distances are 20 ft (a), 10 ft (b), 2 ft (c), and 6 inches (d).*

Figures 4 and 5 show the GSR particle size distributions of the CCI and SuperX cartridges, respectively. The results embodied in Figs. 4 and 5 match what would be expected to be produced by referring to Fig. 3. For both cartridges, the GSR particle sizes increase as the shooting distance decreases. The size distribution as a function of the shooting distance is thereby determined and can be used to estimate an unknown shooting distance by comparing the GSR size distributions of the unknown shooting distance with that of known shooting distances. For the two different cartridges, the GSR particle size distributions with the same shooting distance are not uniform, as can be clearly seen from Figs. 4 and 5. The particle sizes from the SuperX cartridges are smaller than those of the particles from the CCI cartridges with same shooting distance. This is most likely because of differences in the manufacturing process, which is out of the range of this paper. But this reminds us that only results from the same cartridge manufacturer are consistent.

IR (ATR) Spectra of GSR Particles

Gun powders for handguns and rifles are usually composed of nitrocellulose (single base), nitrocellulose and nitroglycerin (double base) along with minor components/additives. Therefore, the common representative functional groups of gun powders include nitro ($-NO_2$) and nitrate ($-NO_3$) (15).

Figure 6*a* shows an ATR spectrum of single-base gun powder from an unfired CCI cartridge, i.e., preshot gun powder, obtained from one of the three cartridges used herein. The spectra of the powder from all three types of cartridges are essentially identical, which suggests that the chemical material compositions of these cartridges are similar. For this reason, only one representative spectrum is shown in Fig. 6*a*. The spectra of the GSR particles resulting from these cartridges at a shooting distance of 6 inches are shown in Figs. 6*b*–6*d*. The spectra exhibit different features which can be utilized to discriminate the cartridge types. The different chemical reactions and ignition degrees during the shooting process can most likely be attributed to the differences in these spectra. It is very difficult to identify the chemicals in the GSR by their ATR spectra considering the complexity of the components of the GSR. Therefore, we only distinguish the functional groups that contribute to the bands in the spectra of these GSR particles. The ATR spectra were collected from measurements on the aluminum foil surface near the bullet hole. Distinct characteristic bands of the CCI GSR (Fig. 6*b*) appear in the range of 2800–3000 cm^{-1}. These bands can be ascribed to the C–H stretching vibrations of saturated $-CH_3$ functional groups (16,17). The bands of the CCI GSR are so sharp and intense that they can clearly discriminate the CCI cartridge from the other two cartridges. The characteristic bands of the SuperX GSR (Fig. 6*c*) (16,17) can be

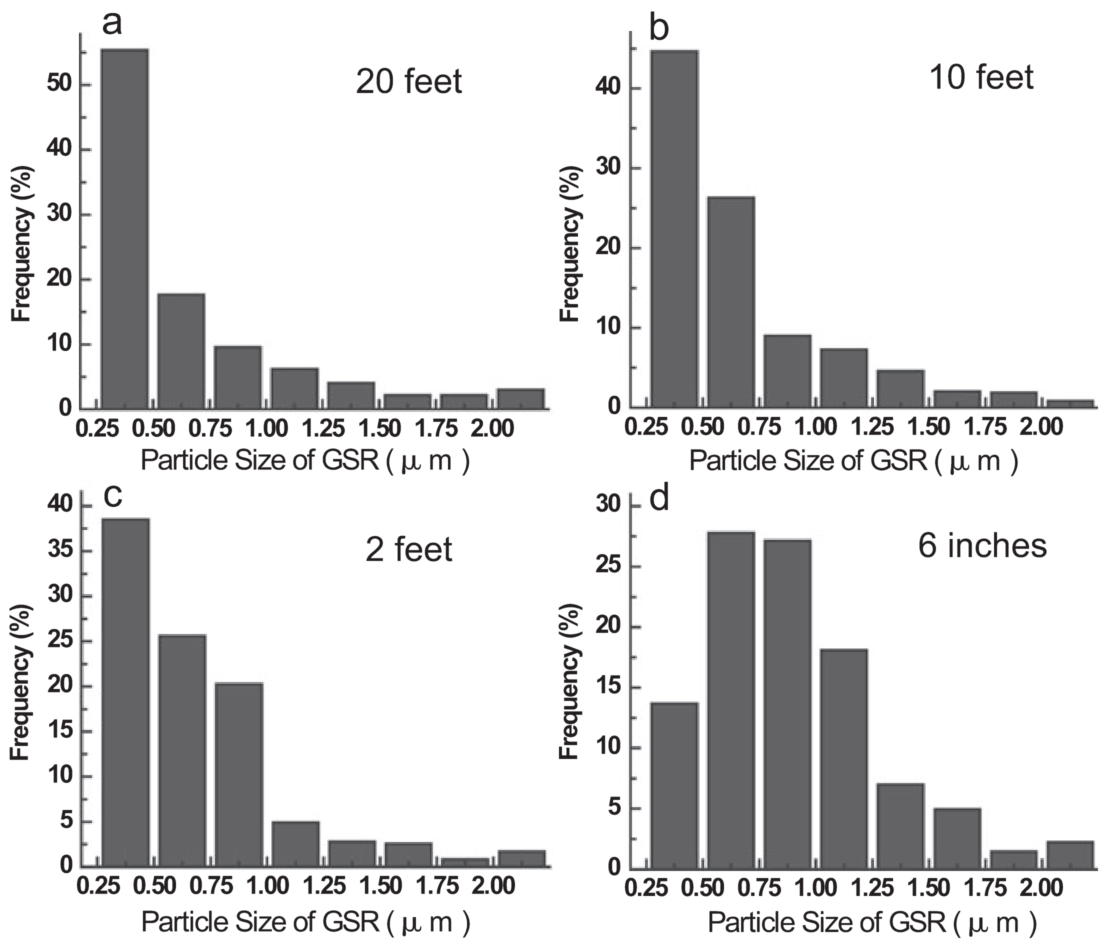

FIG. 5—*GSR particle size distribution of SuperX cartridges with different shooting distances. The shooting distances are 20 ft (a), 10 ft (b), 2 ft (c), and 6 inches (d).*

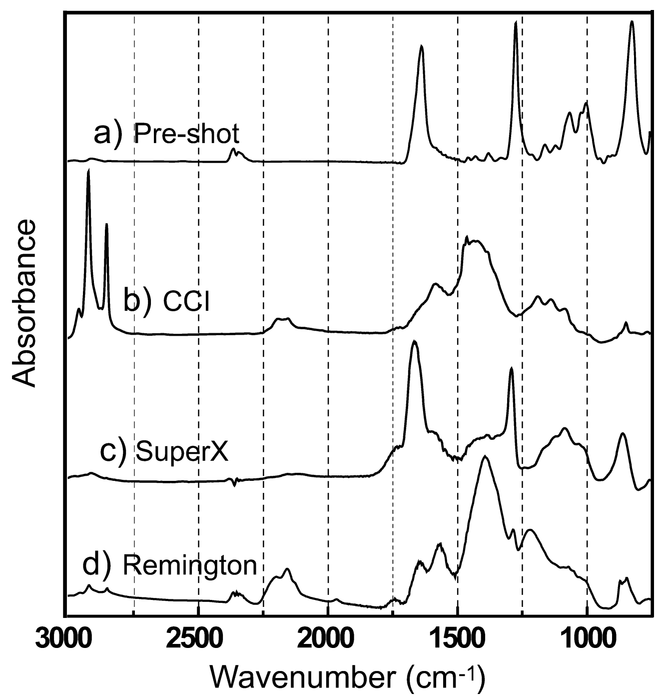

FIG. 6—*ATR spectra of preshot gun powder (a). Spectra of the GSR particles from the three types of cartridges are shown as (b) CCI, (c) SuperX, and (d) Remington.*

assigned to the nitro functional group, i.e., $-NO_2$ asymmetric stretch (1650 cm^{-1}), $-NO_2$ symmetric stretch (1280 cm^{-1}), and $-NO_2$ scissors (850 cm^{-1}). The bands of the Remington cartridge (Fig. 6*d*) at 1390 cm^{-1} and 840 cm^{-1}, which are respectively assigned to N–O stretching and N–O out-of-plane bending of the nitrate group (16,17) can be used to identify the Remington cartridge.

Acknowledgments

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