Pyrotechnic Reaction Residue
Particle Identification by SEM / EDS

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ABSTRACT

Today the most reliable method for detecting gunshot residue is through the combined use of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) of the resulting X-rays. In recent years, this same methodology has found increasing use in detecting and characterizing pyrotechnic reaction residue (PRR) particles. This is accomplished by collecting particulate samples from a surface in the immediate area of the pyrotechnic reaction. Suspect PRR particles are identified by their morphology (typically 1 to 20 micron spheroidal particles) using a SEM, which are then analyzed for the elements they contain using X-ray EDS. This will help to identify the general type of pyrotechnic composition involved. Further, more detailed laboratory comparisons can be made using various known pyrotechnic formulations.

Keywords: pyrotechnic reaction residue, gunshot residue, scanning electron microscopy, energy dispersive spectroscopy, morphology, X-ray elemental analysis, forensics

Introduction

The combined use of scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) for the use in the detection of gunshot residues (GSR) was introduced in the mid-1970's.[1] This GSR analytic method has become so well established that it has been defined through an ASTM standard.[2] In essence, the method uses SEM to identify particles with the correct morphology and X-ray EDS to determine whether those particles have the correct elemental constituents. The sought after GSR particles have a morphology that is nearly spherical in shape and range in the size from approximately 0.5 to 5 microns. These residue particles, which originate from the primer composition, are spheroidal in shape because they are formed at high temperature, where the surface tension of the molten residue droplets contracts them into spheroids before they solidify upon cooling. The particles are relatively small because they are created under near explosive conditions, first at high pressure inside the firearm, then suddenly expanding to atmospheric pressure. The sought after GSR particles most commonly have lead, antimony and barium present (or some combination thereof), often in conjunction with a small collection of other chemical elements. This is because GSR particles have essentially the same elements present as in the formulation used in the primer for the cartridge, where compounds containing lead, antimony and barium are common.[3] In addition, materials from the projectile, cartridge case and barrel of the weapon may be present in GSR particles. The chemical elements present in smokeless powder are the same as are generally present in organic matter and are thus not unique to GSR. (However, these materials can often be chemically detected by other means.[4])

The requirement for both the correct morphology and the correct elemental composition, all within the same individual particle, provides high specificity. Certainly this methodology provides much higher specificity than the previously accepted technique for GSR analysis based

on atomic absorption spectroscopy of washes taken from the hands or clothing of an individual. In fact the SEM / EDS technique is considered so specific that in a recent survey, some forensic laboratories consider finding even a single particle meeting the GSR criteria sufficient to report that a person was near a discharging firearm.[5] (Note, however, essentially all laboratories surveyed did not provide the specific number of particles required for positive GSR identification. Presumably because the answer is more complicated, requiring consideration of things such as whether there may be natural or industrial materials present that have similar attributes.) The same high degree of specificity that SEM / EDS offers in GSR detection, also applies to the identification of pyrotechnic reaction residue (PRR) particles; however, there are two important differences. First, the chemical elements present in PRR particles are mostly different (and potentially more varied) than those most commonly found in GSR. Second, generally the quantity of PRR particles produced is several orders of magnitude greater than that for GSR. The first difference makes performing PRR analysis somewhat more difficult, but the second makes it much easier.

Although using the combination of SEM / EDS is well established from decades of use in GSR analysis, and although the same methodology applies equally well to the analysis of PRR particles, relatively little information regarding its use for PRR particle analysis has appeared in the literature. Most of the articles are recent and in the context of pyrotechnic residues that may be found to meet the criteria of GSR.[6–9] The one exception known to the authors is a single article produced at the Explosive Forensic Laboratory in the UK.[10] This lack of published information is unfortunate, because this is a powerful investigative tool about which too few people are aware. Granted, the number of pyrotechnic and fireworks incidents whose investigations can benefit from this technique is not large. However, in those instances where it can be beneficial, probably no other methodology can produce comparably useful results. Accordingly, this paper was written to increase awareness of the use of SEM / EDS for the analysis of pyrotechnic reaction residues for the purpose of accident investigation. Since many investigators may not be familiar with SEM / EDS, this article includes some basic information about these techniques. However, it should be noted that many details and subtleties of SEM / EDS methodology are beyond the scope of the present article.

Basic SEM / EDS Methodology

Most of what is described in the remainder of this article is independent of the type of instrument used. However, it may be instructive to describe the instrument most often used by the authors. The SEM is a manually operated AMRAY 1000, recently remanufactured by E. Fjeld Co.[11] For this work, the instrument is most often used in the secondary electron mode, but it is occasionally used in the backscatter and spot mapping modes when that is called for. The instrument provides software driven digital imaging. The X-ray spectrometer is energy dispersive, using a Kevex Si(Li) detector[12] with a beryllium window in conjunction with an American Nuclear System[13] model MCA 4000 multichannel analyzer and its Quantum-X software (version 03.80.20). Most typically, samples are collected on conductive carbon dots and are not coated. However, to improve the image quality of some of the micrographs in this article, some specimens were lightly sputter coated with gold. Finally, it should be noted that much additional and more detailed information on the techniques used will be included in a subsequent article.[14]

Much of the information presented in this section is based on standard texts dealing with the subjects of scanning electron microscopy and X-ray energy dispersive spectroscopy.[15,16] In its simplest terms, the operation of a SEM can be described as follows. An electron gun produces high-energy electrons that are focused and precisely directed toward a target specimen in a vacuum (see Figure 1). As a result of this bombardment, among other things, low energy secondary electrons are produced through interactions of the beam electrons with the atoms in the specimen. In the most commonly used SEM mode, these secondary electrons are collected and used to generate an electronic signal. The amplitude of that signal is dependent on the nature and orientation of the portion of the specimen being bombarded at that time. The impinging electron beam can be systematically moved
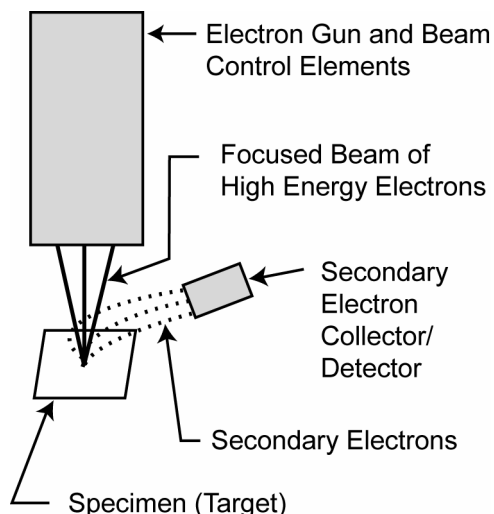
Figure 1. Illustration of some aspects of the production and collection of secondary electrons in a SEM.

Figure 2. Illustration of some aspects of rasterized SEM scanning to produce an image.

over the specimen in a rasterized pattern of scans (see Figure 2). The resulting secondary electron signal can then be used to create an overall (television-like) image of that portion of the specimen being scanned. Because the incident beam of electrons is highly focused and because the pattern of scans across the specimen can be precisely (microscopically) controlled, the image produced is of high spatial resolution and can be highly magnified (easily to 20,000 X).

Along with the production of secondary electrons, much higher energy backscatter electrons are also produced. Because of their high energy, only a relatively few will be detected and can be used for imaging. Nonetheless, there are times, discussed later in this article, when using backscatter electrons for imaging will be a useful tool in identifying the origin of some types of particles found within samples.

In addition to the production of secondary and backscatter electrons, another result of the interaction of the electron beam with the target specimen is the production of X-rays. These X-rays are uniquely characteristic of the type of atoms (the chemical elements) that produced them. By detecting and analyzing the energies of the X-rays that are generated, the identity of chemical elements in the target specimen can be determined.
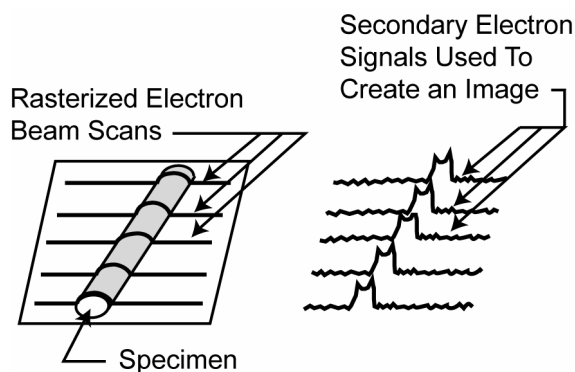
The most common method for analyzing the X-rays produced by the specimen is described as energy dispersive spectroscopy (EDS). This uses a solid state [Si(Li)] X-ray detector. The output of this detector consists of voltage pulses that are proportional to the X-ray energies being deposited. Using a multichannel analyzer (MCA), the signal pulses are sorted according to voltage (energy) and the results stored for subsequent interpretation (i.e., identification of the atomic elements present). There are some limitations on the range of energies of the X-rays that are produced and detected using a SEM / EDS instrument. The maximum energy of the X-rays will be a little less than the energy of the electron beam (which typically is 20 or 30 keV). However, as a practical matter, good X-ray yields require a beam energy at least 1.5 times the X-ray energy. Further, there is an energy threshold below which the X-rays will not be detectable. For those many instruments that use a vacuum isolating beryllium window, this threshold is approximately 0.5 keV. This has the effect of preventing the detection of the X-rays from elements below oxygen in the periodic table. (As a practical matter, for such instruments, X-rays from elements below sodium are difficult to detect.)

As the primary beam of electrons penetrates and interacts with the specimen, there is a loss of their initial energy, and with that, a loss in the electron's ability to stimulate the production of higher energy X-rays. While it depends on the electron beam energy and the nature of the specimen, for the X-ray energies of interest in PRR particle analysis, the depth of interroga-

tion should be considered to be no more than approximately 5 μm.

Accordingly, the combination of SEM / EDS allows (with some limitations) the microscopic imaging of specimens and the determination of the chemical elements present in those specimens. It is this powerful combination of abilities that allows for the rapid identification and characterization of PRR particles.

Pyrotechnic Reaction Residue Particle Morphology

In essentially every case, pyrotechnic reactions produce sufficient thermal energy to produce molten reaction products. Further, in the vast majority of cases, some temporarily vaporized reaction products are also generated—usually along with some permanent gases. Assuming the pyrotechnic reaction is somewhat vigorous, the temporary and permanent gases act to disperse the molten and condensing reaction products as relatively small particles. The size of these residue particles varies from several hundreds of microns down to considerably less than one micron. The distribution of particle size depends on the nature of the pyrotechnic composition and the conditions under which they were produced. Explosions tend to produce only relatively small particles (smoke), whereas mild burning tends to produce a wider particle-size distribution, including many larger particles. Because of surface tension, those pyrotechnic reaction residue (PRR) particles that were molten and then solidified while airborne will generally be spherical (or at least spheroidal) in shape. The collection of electron micrographs in Figure 3 demonstrates the appearance of some PRR particles. The selected particles range from approximately 10 to 20 microns in diameter. These particles were collected from a surface that was one foot (0.3 m) from an explosion produced using a type of fireworks flash powder. In this same test, in addition to particles of pyrotechnic origin, soil particles are present that were mobilized as a result of the explosion. For comparison, see Figure 4, which is a collection of micrographs of typical soil particles of geologic origin. Again, all selected particles range from approximately 10 to 20 microns.
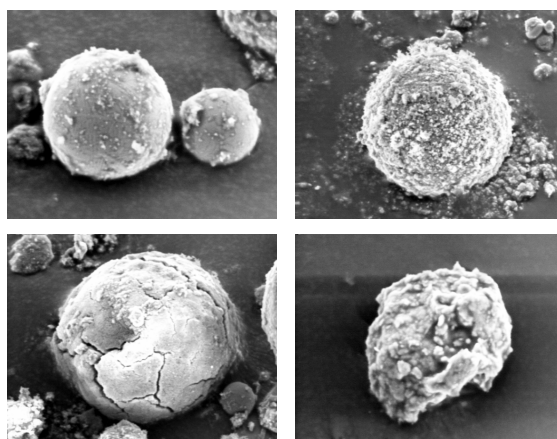

Figure 3. Examples of 10 to 20 micron spheroidal pyrotechnic reaction residue (PRR) particles.
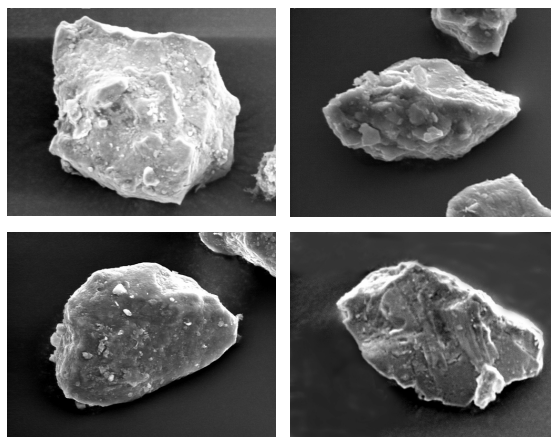

Figure 4. Examples of typical 10 to 20 micron particles of geologic origin (soil).

As illustrated in Figures 3 and 4, most often there are discernable differences between PRR particle morphologies and those of geologic soil particles; however, this cannot be absolutely relied upon. Pyrotechnic residues often include particles that are non-spheroidal, and some geologic particles can be spheroidal. The non-spheroidal particles of pyrotechnic origin can be unreacted components of the pyrotechnic composition or reaction residues that are not spheroidal, apparently the result of their still being molten when they collided with the collection surface. Occasionally soil particles appear nearly spherical in shape, apparently the result of their being mobile in the environment for a long time, during which abrasive action removed their sharp, angular features.

Another potential complication in identifying PRR particles is that occasionally particles of unreacted pyrotechnic composition can be spheroidal in shape. This can be a result of their method of manufacture or processing. For example, the left image in Figure 5 is a type of atomized aluminum occasionally used in pyrotechnic formulations. [17] The right image is a particle of potassium nitrate that has been prepared for use by ball milling to reduce its size.[18] If any particles such as these are left unreacted after an incident, it is possible a few could be found interspersed with PRR particles.
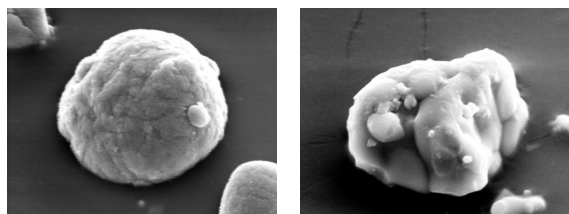

Figure 5. Examples of 10 to 20 micron spheroidal or nearly spherical particles sometimes found in pyrotechnic compositions: left, atomized aluminum; right, ball-milled potassium nitrate.

There are other types of non-pyrotechnic particles that are spheroidal and fall in roughly the same size range as PRR particles. The two images in Figure 6 are examples of spherical particles of biologic origin: blood cells and grass pollen. Although the explanation is beyond the scope of this article, the yield of secondary electrons is virtually independent of atomic number (Z), whereas the yield of backscatter electrons depends highly on the Z of the target atoms, see Figure 7. Accordingly, the use of the backscatter mode of the SEM operation is useful in differentiating between organic particles (low Z) and PRR or geologic particles (typically higher Z). Similarly, in those instances when there is sufficient difference in atomic number between PRR and geologic particles, the use of backscatter mode can be useful. The two images in Figure 8 illustrate the difference between operating in secondary and backscatter electron modes. Note how the two high Z lead particles clearly appear brighter than the many particles of organic material. Finally, Figure 9 demon-
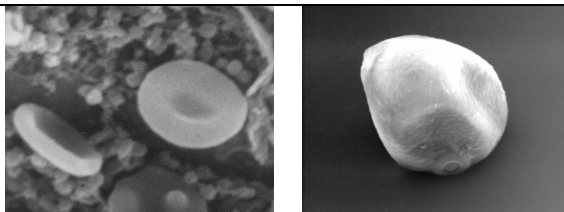

Figure 6. Examples of 5 to 20 micron spheroidal particles of biologic origin: left, red blood cell; right, grass pollen.

strates two more spheroidal particles that can be found in the environment that are of non-pyrotechnic origin. These are a particle produced by grinding metal and a cigarette smoke particle. All these various particle shapes for both PRR and non-PRR particles not withstanding, keying on spheroidal particles for analysis is still quite useful, as this fairly quickly targets those particles that have the best chance of being PRR particles.
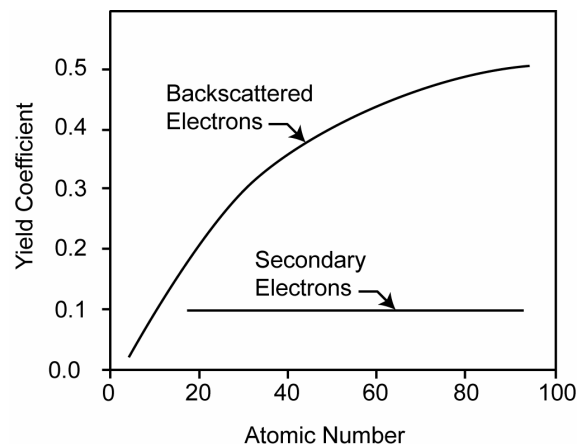

Figure 7. A graph illustrating the number of secondary and backscatter electrons produced from targets as a function of atomic number. (Based on references 15 and 16.)
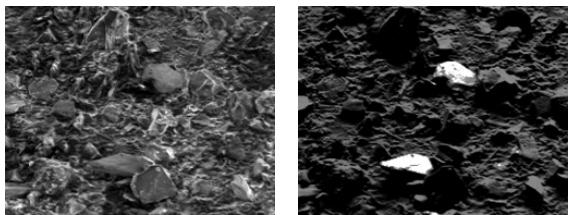
Figure 8. These two images demonstrate the difference between operating the SEM in the secondary electron and backscatter modes with a mixture of organic and high atomic number particles. (This specimen had been coated using a carbon spray.)
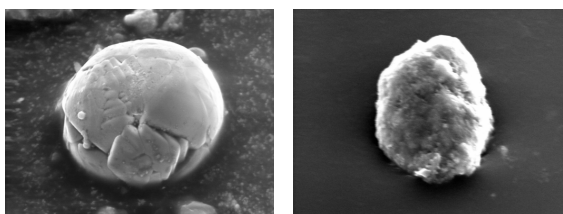

Figure 9. Examples of 10 to 20 micron spherical particles in the environment: left, particle from metal grinding and right, cigarette smoke particle.

Suspect Particle X-ray Signatures

Table 1 is a list of those chemical elements somewhat commonly found in pyrotechnic compositions. Included is an attempt to estimate the relative overall frequency of each chemical element's presence in civilian and/or military compositions. Also included are the energies of the X-ray peaks that are most often used to establish the presence of that element in PRR particles. Because many instruments commonly in use have difficulty detecting X-rays from the elements below sodium in the periodic table, those elements have not been included in Table 1.

Of course, all of the chemical elements present in the unreacted pyrotechnic composition will be present in the combustion products. However, not all of the elements will be present in the solid residues to the same degree that they were in the unreacted composition. For example, when sulfur is used as an ingredient in a high-energy flash powder, it is generally not found in the PRR particles. Most likely this is because it

Table 1. Chemical Elements Most Commonly Present in Pyrotechnic Compositions.

Element and Atomic No. (a)	Z (b)	F/P (c)	X-ray Energies (keV) (d) (e)
Sodium	11	1	1.04
Magnesium	12	1	1.25
Aluminum	13	1	1.49
Silicon	14	2	1.74
Phosphorous	15	3	2.01
Sulfur	16	1	2.31
Chlorine	17	1	2.62
Potassium	19	1	3.31, 3.59
Calcium	20	3	3.69, 4.01
Titanium	22	2	4.51, 4.93
Chromium	24	3	5.41, 5.95
Manganese	25	3	5.90, 6.49
Iron	26	2	6.40, 7.06
Copper	29	1	8.04, 8.90
Zinc	30	3	8.63, 9.57
Strontium	38	1	1.82, 14.14, 15.84
Zirconium	40	2	2.06, 15.75, 17.71
Antimony	51	2	3.60, 3.86, 4.10
Barium	56	1	4.46, 4.84, 5.16
Lead	82	2	2.36, 10.55, 12.62
Bismuth	83	3	2.44, 10.83, 13.02

a) Only those elements producing characteristic X-rays with energies above 1.0 keV are listed. The elements are listed in order of increasing atomic number.

b) Z is atomic number.

c) F/P means the frequency of presence of this element in pyrotechnic compositions. Rankings range from 1 to 3, with 1 indicating those elements most frequently present, and 3 indicating those elements only occasionally present. No attempt was made to differentiate between their presence in civilian versus military pyrotechnics.

d) Energies (in keV, reported to 0.01 keV) for the X-rays between 1 and 20 keV that are most frequently used to identify the presence of the element.

e) When using an energy dispersive X-ray spectrometer, sometimes there will be overlaps of some of the X-rays listed. However, in most instances these cases should not result in their misidentification. This will be discussed in a future article.[14]
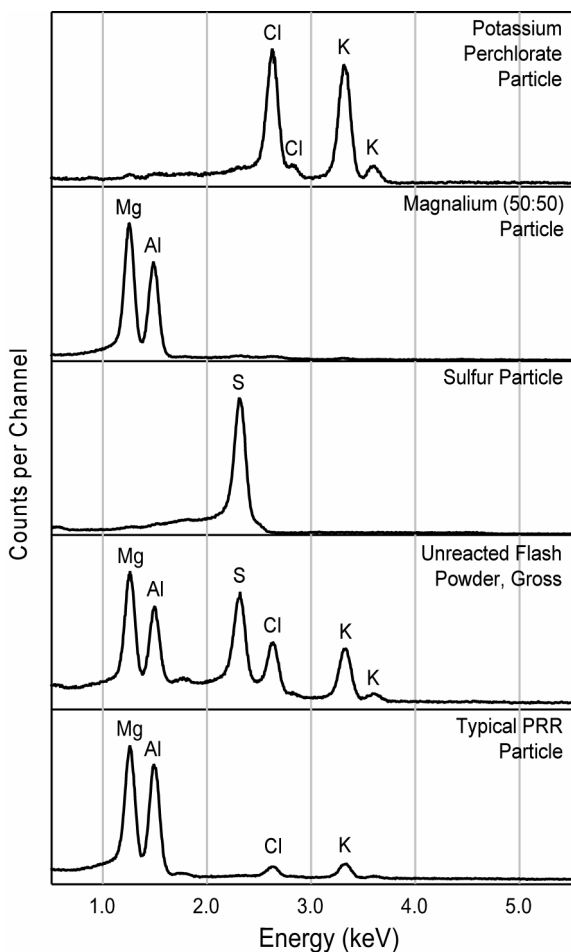
Figure 10. X-ray spectra from a pyrotechnic flash powder.

Figure 11. X-ray spectra produced during an accident investigation.

has reacted to form sulfur dioxide, a gas, which is lost.

In Figure 10, the three upper X-ray spectra are those from individual particles in an unreacted flash powder with the formulation: 60% potassium perchlorate, 30% magnesium:aluminum alloy 50:50 (magnalium), and 10% sulfur. Below them is the spectrum from a "gross" sample of the unreacted flash powder, collected such that the X-rays originate from a large collection of individual particles, and produce a spectrum representative of the average composition of the unreacted flash powder. The lower most X-ray spectrum is typical of that produced by a PRR particle. In the lower two spectra, note the difference in the sulfur peaks; while it is quite prominent in the unreacted gross spectrum, it is missing from the gross residue spectrum. The
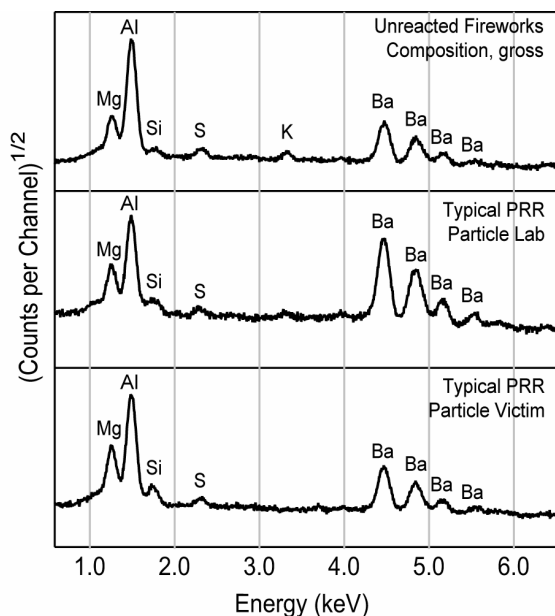
reduction of the potassium and chlorine peaks, and a small change in the ratio of magnesium and aluminum peaks will be discussed in a subsequent article addressing some of the finer points of PRR particle analysis.[14]

The vertical scales of the spectra were normalized such that the largest X-ray peak in each spectrum has the same, full-scale height. This method was chosen because it readily facilitates the comparison of spectra collected for different lengths of time, or for which different count rates were produced. Also, while data was collected to nearly 20 keV, the horizontal (energy) axis was truncated at a point shortly above the last significant X-ray peak found in any spectrum, in this case at about 5.5 keV. This provided a clearer view of the peaks that are present. Similarly, the portion of the spectrum below approximately 0.5 keV was not included.

The X-ray spectra in Figure 11 were produced as part of an accident investigation. In this case, an individual received burns when a firework allegedly exploded and sent burning pieces of pyrotechnic composition in his direction. Uppermost is the gross spectrum of the composition taken from the firework alleged to have been responsible for the injury. In the middle is a spectrum typical of a PRR particle

produced by burning this same pyrotechnic composition under laboratory conditions. Lowermost is a spectrum typical of PRR particles taken from the clothing of the burn victim. In comparing the two lower spectra, note that the spectrum of PRR particles from the victim is consistent with having been produced by the suspect firework.

The spectra in Figure 11 were recorded for a relatively short time, approximately 1.5 minutes. It is often appropriate to use short collection times, from 0.5 to 2 minutes. Generally, data collection time only needs to be sufficient to confidently identify the significant elemental components of the particle. This allows the analysis of a greater number of PRR particles, thus increasing one's confidence in any conclusions reached. When needed, longer data collection times can be used when attempting to identify minor components of a suspect particle.

All of the spectra presented in Figure 11 (and Figure 13) use a vertical scale presenting the square root of the number of counts per channel. This scale was chosen because it readily facilitates the observation of both major and minor X-ray peaks in the spectrum (as well as giving an indication of their statistical precision). As in Figure 10, the vertical scales have been normalized to have the largest peak reach full scale, and the horizontal axis has been truncated at a point a little higher than the last peak observed.

For the most part, those particles of geologic origin, comprising the inorganic components of soil, can be eliminated from consideration based on their non-spheroidal morphology. (See again Figure 4.) In addition, those few geologic particles that appear roughly spheroidal can almost always be eliminated based on their X-ray signatures. To someone without a geochemistry and pyrotechnic chemistry background, this might not be readily apparent, especially after considering Table 2, which lists the abundance of the most prominent chemical elements in the Earth's crust. Note that of the ten most abundant crustal elements, all eight of those with atomic numbers from sodium and above also appear in the list of elements somewhat commonly present in pyrotechnic compositions. The non-morphologic basis for discriminating between geologic and PRR particles is discussed in the next few paragraphs.

Table 2. Average Crustal Abundance.[19]

Element	% (a)	Element	% (a)
Oxygen	46.6	Sodium	2.8
Silicon	27.7	Potassium	2.6
Aluminum	8.1	Magnesium	2.1
Iron	5.0	Titanium	0.4
Calcium	3.6	Hydrogen	0.1

a) Percent by weight, expressed to 0.1%.

Sometimes the presence of pyrotechnic residue is so abundant that it is clearly visible as whitish, grayish or blackish material on the surface of items exposed during the incident. In that case, the samples taken from those locations are likely to contain a relatively high proportion of PRR particles. This combined with the relatively small number of geologic particles that fit the morphology criteria for residues, often allows the tentative identification of residue particles based primarily on statistical considerations. For example, consider the case of examining a total of 50 suspect particles selected because they meet the PRR morphology requirements. Suppose that 40 of these have elemental signatures consistent with being from the same source. Whereas the 10 others have one or another of a few other general signatures. In this case, based on probability alone, it is somewhat likely that the 40 particles are of pyrotechnic origin. The level of confidence significantly increases if the X-ray elemental signature for the 40 particles is consistent with having been produced pyrotechnically (even more so if there is an absence of such particles in background samples, discussed further below). Nonetheless, it must still be considered that some of the 10 other morphologically correct particles may also be of pyrotechnic origin, such as might have been produced in another event or from a different pyrotechnic composition.

Often the exposure to pyrotechnic residues is limited, either in duration of exposure, by distance from the reaction, or both. In addition, it is possible that the surface to be sampled was dirty at the time of the exposure, has become dirty since the exposure, or is of a nature that will produce an abundance of non-pyrotechnic material. In these cases, gross statistical considerations and general pyrotechnic knowledge may

not be sufficient to produce results with a reasonable confidence level. In such cases, or to increase ones general confidence in the identification of residue particles, a combination of two other things will greatly aid in discriminating between PRR particles and those relatively few geologic particles with similar morphologies. First is the taking and analyzing of background samples, which can come from at least three different sources. Background samples can be taken of the soil (dirt) in the local area that is thought to be free of the pyrotechnic residues of interest. Background samples can be taken from the surface of items in the area of the incident, which are similar to those items of interest, but which were far enough away to be reasonably free of the pyrotechnic residues of interest. Background samples can also be taken from the primary items being sampled for PRR particles. In that case, an examination of non-spheroidal particles that clearly appear to be non-pyrotechnic in origin can also be useful in establishing the elemental signatures of geologic particles. Any of these various background samples are useful in establishing a list of elemental signatures for non-pyrotechnic particles that are likely to be found on the suspect items. Then, depending on whether the suspect particles have elemental signatures similar to background geologic particles, their origin can often be established with reasonable confidence. If not, the particles must be considered to be of indeterminate origin, at least until further information is developed.

A great aid in discriminating between geologic and PRR particles is knowledge of the likely elemental signatures for both types of particles. For example, for the most common EDS units, far and away the most abundant geologic element that can be detected is silicon, and the most common mineral is one or another form of quartz, silicon dioxide.[20a] Accordingly, it is not uncommon to find particles that produce essentially only silicon X-rays. Further, it is known in pyrotechnics that: silicon is not one of the more commonly present elements; silicon is primarily used in military formulations; silicon only tends to be used in the igniter portion of a device, which is generally only a tiny portion of the total amount of composition likely to be present; and silicon is essentially always used in combination with other readily detectable elements. Thus, when a particle is examined and found to exhibit only silicon X-rays, even when it has a morphology roughly consistent with PRR particles, one can be relatively certain that it is of non-pyrotechnic origin (especially if such particles have also been found in background samples). A similar argument can be made for particles exhibiting essentially only calcium X-rays, which may be one or another geologic form of calcium carbonate.[20b]

Geologic particles producing combinations of X-rays are a little more problematic, but most can also be identified with a reasonable degree of confidence. For example, feldspar refers to a group of minerals making up about 60% of the Earth's crust.[20c] Most commonly these are combinations of silicon, aluminum, and one or the other of potassium, sodium or calcium. While these specific combinations occur frequently in geologic particles, it would be unusual to find such combinations in PRR particles. Although a little too simplistic to make it a general rule, the most common geologic material will generally have silicon or calcium as the most prevalent X-ray peak, whereas pyrotechnic material will generally have little, if any, of these present. (For more complete information on the forensic analysis of soils using SEM, see reference 21.)

Like particles of geologic origin, those that are organic in nature (biologic or manmade) generally will not have morphologies mistakable for PRR particles. Also, similar to geologic particles, organic particles will have X-ray characteristics that greatly aid in their identification. One of these characteristics is their low rate of production of X-rays with energies greater than 0.62 keV. This is a result of biologic particles being mostly comprised of elements with elements no higher than oxygen. Thus, it is common for biologic particles to produce no more than about 1/3 the number of X-rays above 0.6 keV than will geologic or PRR particles. Further, the elemental signatures of organic particles are likely to be significantly different from PRR particles. Finally, operating the SEM in the backscatter mode offers the potential to discriminate against biologic particles because of the reduced intensity of their images. However, this generally requires applying an electrically conductive coating to the specimen. Fur-
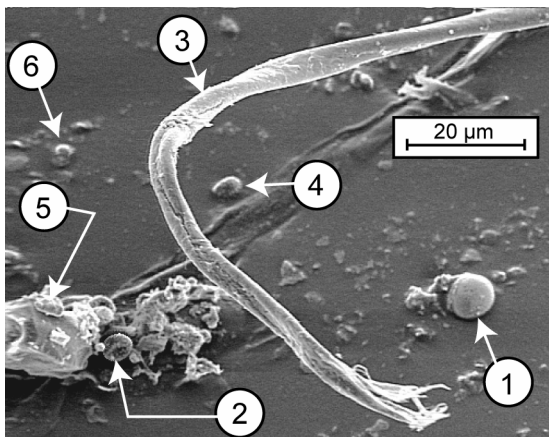
Figure 12. An electron micrograph identifying a series of particles (items) analyzed during an accident investigation. (See Table 3.)

ther, because the difference in Z between organic and geologic or PRR particles is not very great, the image intensity contrast may not be sufficient to allow their easy differentiation.

Generally, it will not be possible to establish the identity and origin of each particle analyzed, and these should be characterized as being "Indeterminate". However, in most cases the sheer number of PRR particles produced is so great (generally at least a thousand times more than for GSR) that there is no need to positively characterize each particle. Further, there is no need for the search for PRR particles to be exhaustive. Rather a statistical approach is taken in which analysis continues only until the degree of certitude reaches the level desired.

Analytical Example

This example comes from the same case mentioned earlier, wherein an individual was burned when a fireworks was alleged to have exploded sending pieces of burning pyrotechnic composition in his direction. Figure 12 is an electron micrograph of a small portion of a sample taken from the inside the individual's clothing, from the general area where the burn occurred. (This specimen was sputter coated with a thin layer of gold to help produce a satisfactory image for publication.) In this image, a series of six items are identified for use as examples of the way the analysis was performed. (In the actual investiga-
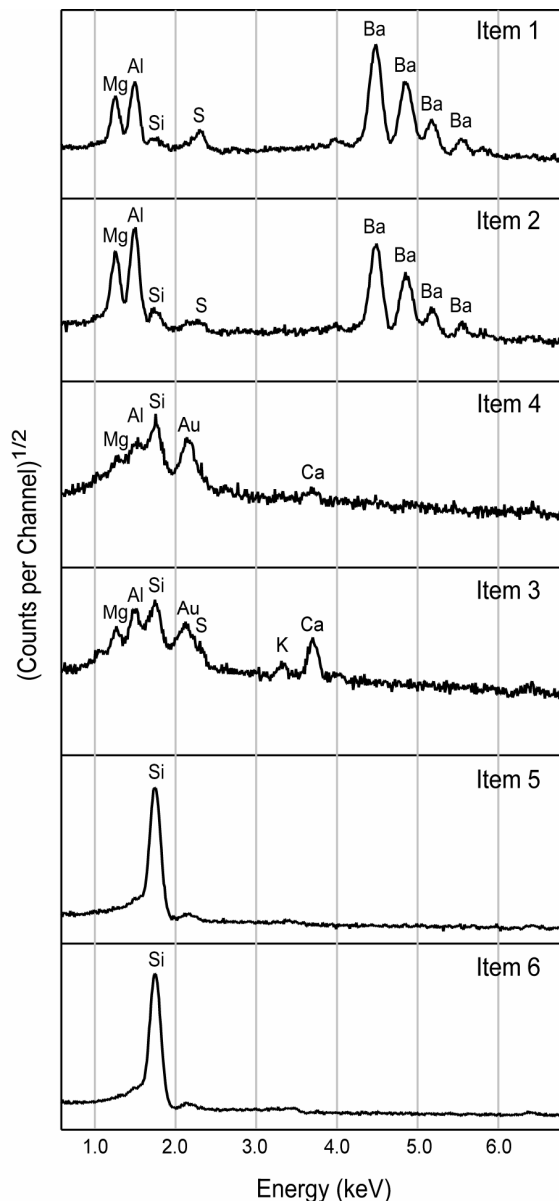

Figure 13. X-ray spectra collected from the six particles identified in Figure 12.

tion, several additional particles seen in this image were also analyzed, as well as many other particles from other portions of this and other samples.) Figure 13 is the collection of the X-ray spectra collected from the six particles (items) identified in Figure 12.

Table 3 presents the results from the analysis of the particles identified in Figure 12 and illustrates a typical methodology used in performing an analysis of PRR particles. However, the categories and classifications will often need to be

Table 3. Analytical Results for the Particles Identified in Figure 9.

Particle Num- ber	Morphology Type	Dead Time (%)	Peak-to- Background Ratio	Chemistry Type	Particle (Item) Identification
1	Spheroidal	16	3.8	Pyrotechnic	PRR Particle
2	Spheroidal	18	3.4	Pyrotechnic	PRR Particle
3	Fibrous	4	1.0	Organic	Organic
4	Indeterminate	4	0.8	Indeterminate	Non-PRR
5	Non-Spheroidal	12	13.	Geologic	Geologic
6	Spheroidal	14	16.	Geologic	Geologic

adjusted for specific investigations. In Table 3, particle *Morphology Type* is basically divided into two categories, *Spheroidal* (in this case meaning near spherical) and *Non-Spheroidal*, with *Fibrous* as a subcategory of non-spheroidal. The reason for including the fibrous subcategory is that organic materials (both biologic and manmade) often have this appearance, while PRR particles do not. (In this example, since the specimen was taken from clothing, many fibrous items were found.) When the appropriate category for a particle is not reasonably clear, it is assigned as being *Indeterminate*.

Multichannel analyzer (MCA) *Dead Time* is the percent of time the MCA is occupied sorting the electronic pulses from the X-ray detector. All things being equal, MCA dead time is a useful indication of the rate at which X-rays from the specimen are being detected. For many systems, the X-rays from elements with atomic numbers (Z) less than approximately 11 (sodium) are essentially not detected. Nevertheless, MCA dead time will often provide a useful indication of the extent to which the specimen is composed of elements with Z less than 11. This is of interest because it will aid in determining whether a particle is organic in nature (whether manmade or biologic). Many things affect the rate of production and detection of X-rays from the specimen. However, for the instrument and the configuration used in this article to produce the spectra in Figure 13, when the dead time is less than approximately 5 percent, it is likely that the vast majority of the atoms in the portion of the specimen being scanned have atomic numbers less than 11. For this reason, spectra dead times have been included in Table 3. As further indication that a recorded spectrum is

from organic material, it will generally not contain any peaks of major intensity. Usually a visual inspection of the spectrum is sufficient to reveal this; however, for the purpose of this example, a quantitative measure of the peak-to-background ratio for the most prominent peak(s) in the spectrum was produced. For the instrument and its configuration used in this article, purely organic material generally produces peak-to-background ratios less than 2. Thus, as a further aid in characterizing particles, Table 3 includes the value for the maximum peak-to-background ratio found in each spectrum.

While the use of approximate MCA dead times to infer something about the predominant atomic numbers of a particle is useful, it is not completely reliable. Even for the same instrument, operated under the same conditions, there are a number of factors that can give false low dead times. For example, for the very smallest particles (those significantly less than the interrogation depth of the electron beam) the count rate (dead time) will be reduced. Similarly, when there is shadowing of the X-ray detector by another portion of the specimen, the count rate will be reduced. These effects are expected and manageable; however, a more complete discussion must be deferred to a subsequent article.[14] Similarly, peak-to-background ratios are not a completely reliable indicator of prevalent atomic number. When there is a mixture of several moderate to high Z materials in the particle, such that there are many prominent peaks in the spectrum, peak-to-background ratios are reduced (in Table 3, compare particles 1 and 2, with particles 5 and 6). Further, sometimes particles are mixtures of organic material with other material having higher Z components. For example, white

paper has calcium carbonate added to make it whiter and more opaque, and organic material may have inorganic material imbedded within or adhering to its surface.

Identification of organic particles can often be aided using the instrument in the backscatter electron mode. However, this is also not always reliable. If there is not a sufficient difference between the atomic number of the PRR and organic particles, the difference in the backscatter yield coefficients may not be sufficient. In that case, the contrast between PRR and organic particles may not be readily apparent given the normal variation in contrast between particles in the image (flaring or excessive contrast), especially when the sample has not been coated.

In Table 3, particle *Chemistry Type* is basically divided into two categories (*Pyrotechnic* and *Non-Pyrotechnic*, with subclasses of *Organic* and *Geologic* for non-pyrotechnic particles). Assignments are made based on the types and ratios of chemical elements present. For the most part, the basis for assigning particles (items) to these classifications was described in the previous section on X-ray signatures. Another non-pyrotechnic subclass is often used for particles that are removed from the substrate from which the sample was collected. This might include paint flecks from a painted surface or rust particles from an iron or steel surface. In the example being discussed, clothing fibers could have been assigned to that category. When the appropriate category for a particle is not reasonably clear, it is assigned as being *Indeterminate*.

Particles one and two, have the correct morphology and reasonably high count rates. Further, their chemistry is consistent with that of a PRR particle, which has been confirmed through the production of effectively identical (matching) PRR particles in the laboratory using the suspect pyrotechnic composition (see again Figure 11). Further, many more particles with the same elemental signature were found in the same area of clothing where the injury occurred. Finally, no similar particles were found on background areas of clothing remote from the area of the injury. Accordingly, with a high degree of confidence, particles one and two are identified as PRR particles.

Item three has the obvious appearance of a fiber; most likely from the individual's clothing itself. Further, its counting dead time and peak-to-background ratio are quite low, suggesting it consists mostly of low Z atoms, and its chemistry is essentially devoid of those major elements associated with geologic or pyrotechnic materials. Accordingly, with a high degree of confidence, this item is identified as being organic material. (The presence of an X-ray peak from gold is the result of the specimen having been sputter coated with gold for the purpose of facilitating the taking of a high resolution electron micrograph for this article. The same gold X-rays were produced by all of the particles being analyzed; however, when those particles produce higher X-ray count rates, the gold peak becomes much less prominent.) Particle four is roughly spheroidal, although it is elongated with a fairly pointed end. Accordingly, it has been conservatively designated as having a morphology that is indeterminate. Its counting dead time and peak-to-background ratio are quite low, suggesting it consisted of mostly of low Z atoms. While its chemistry appears to be much like that of particle (item) three, it has been conservatively designated as indeterminate because of the somewhat increased prominence of X-ray peaks most consistent with geologic material (calcium, silicon, magnesium and aluminum). Taking everything into consideration, with a reasonable degree of confidence, this particle could have been identified as being organic in nature; however, it was more conservatively designated as being *Non-PRR*.

Particle five is of non-spheroidal morphology, has a relatively high dead time, has a very high peak-to-background ratio, exhibits chemistry consistent with being silica sand, and has a chemistry that is quite inconsistent with being pyrotechnic. Further, samples taken from the cuff area of the clothing, well beyond the area of likely deposition of PRR particles contain many particles of the same chemistry. Accordingly, with a high degree of confidence, this particle is identified as being of geologic origin. Except for its spheroidal shape, particle six is like that of particle five. However, geologic particles, that have been mobile in the environment for a prolonged time, tend to become near spherical in shape. Accordingly, with a high degree of

confidence, this particle is also identified as being of geologic origin.

In the case of this example, most of the particles cataloged were not PRR particles. As a practical matter, during an investigation it would be unusual to bother to document the nature of a high percentage of non-PRR particles. Typically, only enough of these particles would be analyzed and documented such as to reasonably represent the range of different non-PRR particles found. Instead, most of the time would be devoted to finding and analyzing PRR particles. In this way, while a few particle assignments may be less than certain, collectively, conclusions can be drawn with a high degree of confidence.

Conclusion

The use the SEM / EDS methodology to analyze PRR particles in the course of investigating accidents involving pyrotechnic materials can provide information with a degree of sensitiveness and specificity that is unavailable with other commonly used techniques. Given the wide spread availability of SEM / EDS instruments and the long history of the successful use of the same methodology in GSR analysis, it is somewhat surprising that the technique is not used more often in investigating accidents involving pyrotechnics. Obviously one reason for its infrequent use is that most accident investigations would benefit little, if any, from the type of information that could be developed. However, even for those accidents where PRR particle analysis would be of great benefit, often that analysis is not performed. After speaking with pyrotechnic researchers and investigators, the authors have conclude the likely reason for its under use is simply that many investigators working outside of forensics are not sufficiently aware of the PRR particle analysis methodology and the information it can provide. Therein lies the purpose of this introductory article, to disseminate some basic information about PRR particle analysis to the scientifically oriented pyrotechnic community. Toward this same end, at least two additional articles are planned. One article will present much more information about the mechanics of specimen production, collection, and their subsequent analysis.[14] A second article will further demonstrate the nature and utility of the information produced by considering a series of investigations of actual and staged incidents.

References

1) R. S. Nesbitt, J. E. Wessel, and P. F. Jones, "Detection of Gunshot Residue by Use of the Scanning Electron Microscope", *Journal of Forensic Science*, Vol. 21, No. 3 (1976) pp 595–610.

2) ASTM: E 1588-95, "Standard Guide for Gunshot Residue Analysis by Scanning Electron Microscopy / Energy-Dispersive Spectroscopy", ASTM, 1995.

3) J. S. Wallace, "Chemical Aspects of Firearms Ammunition", *ATFE Journal*, Vol. 22, No. 4 (1990) pp 364–389.

4) H. H. Meng and B. Caddy, "Gunshot Residue Analysis—A Review", *Journal of Forensic Science*, Vol. 42, No. 4 (1997) pp 553–570.

5) R. L. Singer, D. Davis, and M. M. Houck, "A Survey of Gunshot Residue Analysis Methods", *Journal of Forensic Sciences*, Vol. 41, No. 2 (1996) pp 195–198.

6) P. V. Mosher, M. J. McVicar, E. D. Randall, and E. H. Sild, "Gunshot Residue-Similar Particles by Fireworks", *Canadian Society of Forensic Science Journal*, Vol. 31, No. 2 (1998) pp 157–168.

7) J. R. Giacalone, "Forensic Fireworks Analysis and Their Residue by Scanning Electron Microscopy / Energy-Dispersive Spectroscopy", *Scanning*, Vol. 20, No. 3 (1998) pp 172–173.

8) P. Mosher, "Fireworks as a Source of Gunshot Residue-Like Particles: An Overview", *Proceedings of the 4th International Symposium on Fireworks* (1998) pp 275–281.

9) J. R. Giacalone, "Forensic Particle Analysis of Microtrace Pyrotechnic Residue", *Scanning*, Vol. 21, No. 2 (1999) pp 100–101.

10) S. A. Phillips, "Analysis of Pyrotechnic Residues—Detection and Analysis of Characteristic Particles by SEM / EDS", *Proceedings of the 2nd European Academy of Forensic Science Meeting, Sept. 2000*.

11) E. Fjeld Co., N. Billerica, MA, USA.

12) Kevex, Inc. Foster City, CA, USA.

13) American Nuclear Systems, Inc., Oak Ridge, TN, USA.

14) K. L. & B. J. Kosanke and R. C. Dujay, "Analysis of Pyrotechnic Reaction Residue Particles Using SEM / EDS", in preparation.

15) J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, A. D Roming, C. E. Lyman, C. Fiori, and E. Lifshin, *Scanning Electron Microscopy and X-Ray Microanalysis*, 2nd ed., Plenum Press (1992).

16) R. E. Lee, *Scanning Electron Microscopy and X-Ray Microanalysis*, Prentice Hall (1993).

17) K. L. & B. J. Kosanke and R. C. Dujay, "Pyrotechnic Particle Morphologies – Metal Fuels", *Journal of Pyrotechnics*, Issue 11 (2000) pp 46–52.

18) K. L. & B. J. Kosanke and R. C. Dujay, "Pyrotechnic Particle Morphologies – Low Melting Point Oxidizers", *Journal of Pyrotechnics*, Issue 12 (2000) pp 5–15.

19) D. L. Holmes, *Holmes Principles of Physical Geology*, John Wiley (1978) p 46.

20) *Van Nostrand's Scientific Encyclopedia*, 5th ed., Van Nostrand-Reinhold (1976), [a] p 1857; [b] p 400; [c] p 1012.

21) M. J. McVicar, "The Forensic Comparison of Soils by Automated Scanning Electron Microscopy", *Canadian Society of Forensic Science Journal*, Vol. 30, No. 4 (1997) pp 241–261.