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Characterization of Pyrotechnic Reaction Residue Particles by SEM/EDS

ABSTRACT: Today the method commonly used for detecting gunshot residue is through the combined use of scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). In recent years, this same methodology began to find use in detecting and characterizing pyrotechnic reaction residue (PRR) particles whether produced by explosion or burning. 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 μm spheroidal particles) using an SEM; then they are analyzed for the elements they contain using X-ray EDS. This can help to identify the general type of pyrotechnic composition involved.

KEYWORDS: forensic science, pyrotechnic reaction residue, gunshot residue, scanning electron microscopy, energy dispersive spectroscopy, morphology, X-ray elemental analysis

The combined use of scanning electron microscopy (SEM) and X-ray energy dispersive spectroscopy (EDS) for use in the detection of gunshot residues (GSR) was introduced in the mid-1970s (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 locate particles with the correct morphology and X-ray EDS to determine the elemental constituents of those particles. The sought-after GSR particles typically have a morphology that is nearly spherical in shape, range in size from approximately 0.5 to 5 μm, and principally originate from the primer composition of a cartridge. Accordingly, 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 (2,3).

Pyrotechnic materials are mixtures of chemical elements and compounds that are capable of undergoing self-contained and self-sustained exothermic reactions for the production of heat, light, gas, smoke, or sound (4). Black Powder, fireworks compositions, safety match composition, and solid rocket propellants are all examples of pyrotechnic materials. In the process of burning or exploding, pyrotechnic materials produce residues, many of which have physical characteristics similar to GSR and that can be detected and analyzed using a similar methodology. The requirement for both the correct morphology and the correct elemental composition within an individual GSR particle provides high specificity, and this same high degree of specificity generally also applies to the identification of pyrotechnic reaction residue (PRR) particles. However, there are three important differences. First, the assemblage of chemical elements typically present in PRR particles is different and often more varied than those most commonly found in GSR. Second, to a greater extent than with GSR, the elements that are present in pyrotechnic residues are also found in other (non-pyrotechnic) materials. Third, the quantity of PRR particles produced during an event is generally several orders of magnitude greater than that for GSR.

As with GSR analysis, the level of certainty of conclusions reached using PRR particle analysis is increased when additional confirmatory data are available. This might include: things as simple as just knowing an explosion occurred in the immediate area and comparisons with background samples, correlating PRR particle-analysis data with conventional analytical chemistry, and interpreting PRR particle-analysis results in the context of known pyrotechnic compositions and the reaction products that would be produced upon their reaction (burning or explosion).

Although using the combination of SEM/EDS is well established from decades of use in GSR analysis, and although the same methodology applies to the detection and analysis of PRR particles, relatively little information regarding its use for PRR particle analysis has appeared in the literature. Most of the papers are recent and in the context of PRR particles that may be found to meet the criteria of GSR (5–9). The only exceptions known to the authors are a paper produced at the Forensic Explosives Laboratory in the United Kingdom (10); an introductory paper by the authors of this paper, written for pyrotechnic researchers with little or no practical knowledge of GSR analysis or SEM/EDS techniques (11); and a compilation of data on the PRR particles produced by consumer fireworks (12). The lack of published information about PRR particle analysis is unfortunate, because for those cases potentially involving pyrotechnic residues, this can be a useful investigative tool about which too few forensic analysts are aware. The purpose of this paper is hopefully to increase awareness of PRR particle analysis and to provide some general information about that methodology.

SEM/EDS Equipment Used

The SEM used in this work was a manually operated AMRAY 1000, recently remanufactured by E. Fjeld Co. (N. Billerica, MA). For this work, the instrument is most often used with an accelerating potential of 20 kV and operated in the secondary electron mode.

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The instrument provides software-driven digital imaging. The X-ray spectrometer is energy dispersive, using a Kevex Si(Li) detector with a 7.6-μm beryllium window, used in conjunction with an American Nuclear System model MCA 4000 multichannel analyzer and their Quantum-X software (version 03.80.20). A 200-μm final aperture was used with a condenser lens setting that produced a spot size estimated to be a little less than 0.4 μm and provided approximately 3 nA specimen current. (Imaging for this paper used a 100-μm final aperture.) Most typically, samples are collected on conductive carbon dots and are not carbon or sputter coated. (However, to improve the image quality of some of the micrographs in this paper, some specimens were sputter-coated with gold.)

In the spectra reproduced for this paper, the vertical scales were normalized such that the largest X-ray peak in each spectrum has the same, full-scale height. Also, while data were collected to nearly 20 keV, the horizontal (energy) axis was truncated at a point shortly above the last significant X-ray peak. Similarly, the portion of the spectrum below approximately 0.5 keV was not included. These changes more clearly display the spectral regions of interest for this paper.

Pyrotechnic Reaction Residue (PRR) Particles

In essentially every case, pyrotechnic reactions produce sufficient thermal energy to produce molten reaction products. In the vast majority of cases, some combination of permanent gases and temporarily vaporized reaction products are also generated. Assuming the pyrotechnic reaction is somewhat vigorous, the permanent and temporary gases act to disperse the molten and condensing reaction products as relatively small particles. The size of these residue particles can vary from more than a millimeter down to considerably less than 1 μm, with those in the range from 1 to 20 μm most often chosen for PRR analysis. The distribution of particle size depends on the nature of the pyrotechnic composition and the conditions under which they are produced. Explosions tend to produce mostly relatively small particles (smoke), whereas relatively mild burning tends to produce a wider particle-size distribution, including many much larger particles. Surface tension causes those PRR particles that were molten while airborne to become spherical (or at least spheroidal) in shape. The electron micrographs in Fig. 1 demonstrate the appearance of some PRR particles.

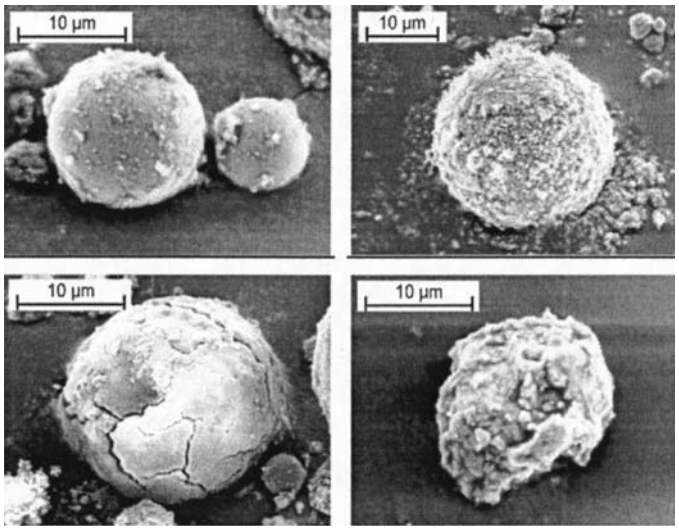

FIG. 1—*Examples of spheroidal pyrotechnic reaction residue (PRR) particles illustrating a range of their appearance.*

TABLE 1—*Chemical elements most commonly present in pyrotechnic compositions.*

Element*	F/P†	Element	F/P†
Sodium	1	Manganese	3
Magnesium	1	Iron	2
Aluminum	1	Copper	1
Silicon	2	Zinc	3
Phosphorous	3	Strontium	1
Sulfur	1	Zirconium	2
Chlorine	1	Antimony	2
Potassium	1	Barium	1
Calcium	3	Lead	2
Titanium	2	Bismuth	3
Chromium	3		

* 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.

† F/P means the "frequency of presence" of this element in pyrotechnic compositions. Rankings are based on the authors' experience and a large collection of pyrotechnic reference texts. The 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.

In this case, the particles ranged from approximately 5 to 20 μm in diameter.

Although the fraction of diagnostic particles to non-diagnostic particles is generally much higher than is found when doing GSR work, often the absolute number of PRR particles is still quite low. Accordingly, as with GSR, it is appropriate to use morphology as an aid in selecting particles for further analysis.

Before leaving the subject of PRR particle morphology, it is important to mention that, while in essentially every instance some spherical particles will be produced during pyrotechnic reactions, often much of the pyrotechnic residue produced will collect as large nondescript masses of once molten slag or dross. This is especially true for slow-burning compositions, compositions that do not form gaseous reaction products, and especially when those reactions occur as burning within an unexploded container of some sort. (To help emphasize that much of the pyrotechnic reaction residue can be in the form of massive slag, and not in the form of tiny spherical particles, this text has adopted the formalism of referring to them as PRR particles.) In cases where pyrotechnic reaction slag is present, collecting and analyzing that slag using conventional chemistry will generally provide the best information about the nature of the unreacted pyrotechnic composition. However, even in such cases, the collection and analysis of PRR particles can aid in identifying items and persons present in the immediate area at the time of the incident. A careful analysis of the distribution of such PRR particles may also allow one to determine details of the nature and course of an incident that are not apparent using other means.

Table 1 is a list of chemical elements often found in pyrotechnic compositions. Included in the table is an estimate of the relative overall frequency of each chemical element's presence in civilian and/or military compositions. Because many EDS instruments have difficulty detecting X-rays from the elements before sodium in the periodic table, those elements have not been included in Table 1. Note that while lead, barium, and antimony compounds are used in pyrotechnics, their use is not particularly common and only extremely rarely have all three elements been found to be present in the same pyrotechnic composition (5–9,12,13). Further, even when some combination of lead, barium, and antimony are present in PRR particles, often elements of much lower atomic number predomi-

nate in the PRR particles. Accordingly, unlike when working with GSR particles, one cannot rely on there being significant backscatter electron brightness contrasts between PRR and non-PRR particles to facilitate locating them. For this reason, most commonly the instrument is operated in the secondary electron mode.

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. Permanent gases produced in the reaction will be lost, and minor components may become concentrated in PRR particles because of their separation from other components during the pyrotechnic reaction. (This is discussed below in the context of PRR particles from a flash powder.) A further complication in comparing reacted and unreacted pyrotechnic materials can be the difficulty in preparing samples for semi-quantitative EDS comparisons. Differences in the physical properties of the components of pyrotechnic compositions (particle size, shape, and density) can result in specimens that do not accurately represent of the element ratios of those pyrotechnic compositions.

In Fig. 2, the three upper X-ray spectra (1–3) 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. Spectrum (4) is from a *gross* sample of the unreacted flash powder, collected such that the X-rays originate from a large collection of individual particles. This is intended to produce a spectrum that is representative of the average composition of the unreacted flash powder. Next is an X-ray spectrum (5) typical of those produced by PRR particles in the range of 5 to 20 μm resulting from the burning of this flash powder composition. In Spectra 4 and 5, note the difference in the size of the sulfur peaks; while it is quite prominent in the unreacted gross spectrum (4), it is missing from the typical PRR spectrum (5). Almost certainly, this is the result of the sulfur reacting to form sulfur dioxide gas, which does not condense to become part of the PRR particles. (It should not be assumed that there would always be similar reductions in the presence of sulfur peaks for other pyrotechnic compositions. In many cases, sulfur reacts to form sulfides and sulfates that remain in the residues. Black Powder is a prime example of where sulfur persists in PRR particles.)

The reduction of the potassium and chlorine peaks between Spectra 4 and 5 is more complicated to explain, but it demonstrates the approach to properly interpret PRR particle results. In this case, the reduction is the result of differences in the physical properties of the condensing reaction products. A simplified chemical equation listing the principal reaction products for this flash powder is

$$KClO_4 + 2\,(Mg/Al) + S + 1.5\,O_{2(air)} \rightarrow KCl + 2\,MgO + Al_2O_3 + SO_2$$

(Note that this chemical equation is only approximate and has not been adjusted for the exact molar quantities of the flash powder formula.)

Table 2 lists the melting and boiling points for the principal products of this reaction. Free energy minimization chemical calculations confirm that these reaction products will initially be vaporized at the completion of the reaction. As the vapor cloud expands after the explosion, it quickly cools and the metal oxides first condense, then solidify. Because of potassium chloride's lower boiling point (sublimation temperature), the metal oxides solidify before any of the potassium chloride can condense. As a result, the potassium chloride associated with the metal oxide particles is found to have been deposited on the surface of the metal oxide PRR particles. This is readily confirmed by exposing the particles to moisture, which dissolves the highly soluble potassium chloride from their surface to leave the insoluble metal oxide core. The ease and extent to which moisture acts to remove the potassium chloride can be seen by examining Spectra 5 and 6 in Fig. 2. The difference between these spectra is that the particle in Spectrum 6 had been exposed to moderate dew, which was sufficient to wash essentially all of the potassium chloride from the surface of the PRR particle.

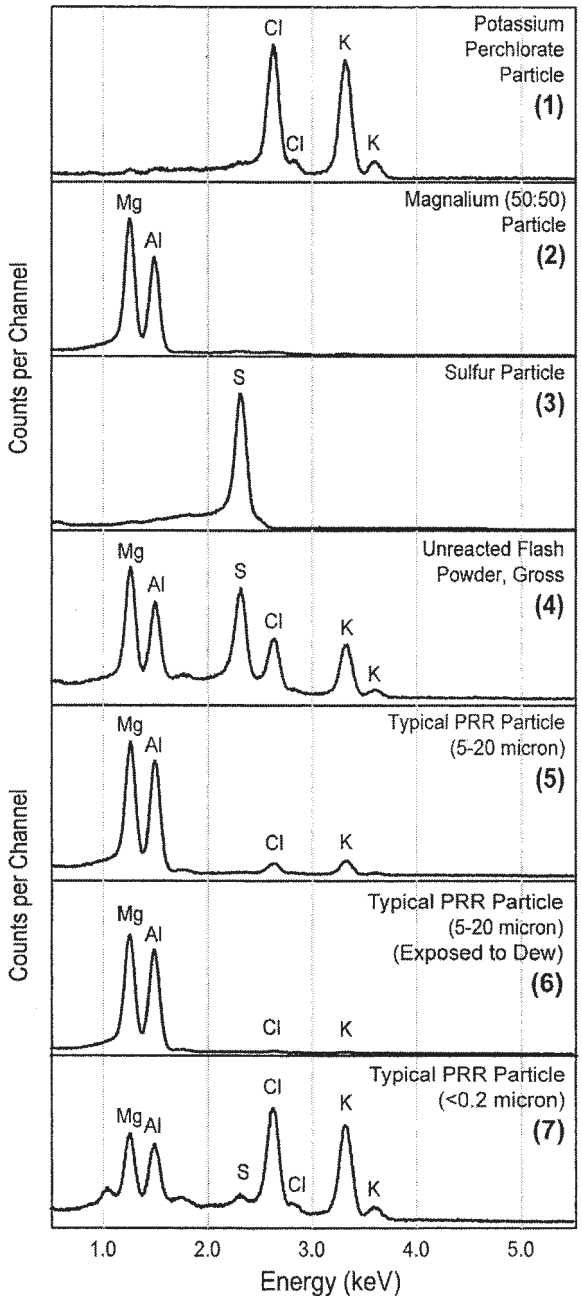

FIG. 2—*X-ray spectra associated with a pyrotechnic flash powder. Spectra 1 through 4 are from individual particles of the components of the unreacted flash powder and a mixture of a large number of particles representing the mixture. Spectra 5 through 7 are from PRR particles of various size and condition.*

Another result of the potassium chloride condensing relatively late in the cooling process explains the reduction of potassium and chlorine peaks in Spectrum 5 as compared with Spectrum 4 in Fig. 2. It is reasoned that, because the larger PRR particles tend to remain hot longer, the potassium chloride is predominantly found to be as-

TABLE 2—*Flash powder reaction products.*

Reaction Product	Temperature (°C)*	
	Melting	Boiling
KCl	770	1500†
MgO‡	2852	3600
Al_2O_3‡	2072	2980
SO_2	1069	1689

* Melting and boiling point temperatures are from Ref 14.

† Note that while KCl has a reported melting point, its vaporization is nonetheless characterized as subliming rather than boiling (14).

‡ For simplicity, MgO and Al_2O_3 are listed as the reaction products; however, the authors analysis by X-ray diffraction indicates that much of the crystallized reaction product is actually $MgAl_2O_4$, which has a melting point of 2135°C (14).

sociated with the smallest particles. This can readily be seen in a comparison of Spectra 5 and 7 in Fig. 2, where Spectrum 7 is typical of particles that are less than approximately 0.2 μm in diameter.

In addition to the variability that can exist in the chemistry of individual PRR particles as a function of their size, there are other sources of systematic and random variability. In some cases, there seems to be relatively small systematic differences in the chemistry (relative quantity of different reaction products) as a function of distance from the pyrotechnic reaction. These changes are on the order of 10 to 20% and are thought to possibly reflect the reduction in temperature within the cloud of condensing reaction products that must occur as the distance from the initial reaction site increases. However, these systematic variations are difficult to observe because of rather large random variations in individual PRR particle chemistry. For example, for the flash powder example discussed above, the one sigma coefficient of variation in the ratio of magnesium to aluminum peaks is approximately 20 to 40% depending on conditions. (Recall that the magnesium and aluminum are present in the pyrotechnic composition as an alloy and not as individual magnesium and aluminum particles. Accordingly, it might have been expected that their ratio in PRR particles would be nearly constant.) While not an area that has been well studied, it seems apparent that the processes at work in the condensing cloud of pyrotechnic residues is such that a large degree of variability from one PRR particle to the next must be expected.

Particle Identification

Sometimes the presence of pyrotechnic residue is so abundant that it is clearly visible as a whitish, grayish, or blackish collection of material on the surface of items exposed during the incident. In that case, samples taken from those locations will contain an exceptionally high proportion of PRR particles. This, combined with the relatively small number of non-PRR particles that fit the morphology criteria for residues, often allows the tentative identification of residue particles based primarily on statistical considerations alone. For example, consider the case of examining a sample collected from such a PRR particle-rich item. Of the first 50 suspect particles selected—because they meet the PRR morphology requirements—suppose that 45 of these have elemental signatures consistent with being of pyrotechnic origin and from the same source. In this case, based on probability alone, it is fairly likely that the 45 particles are from the pyrotechnic event being investigated. (Of course, one's level of confidence increases if the X-ray elemental signature for those 45 particles is not found to be associated with background sources.)

The exposure of items to pyrotechnic residues is often more limited, either in the duration of exposure, by distance from the event, or both. In addition, there are all of the potential difficulties associated with the recovery of GSR. (However, these difficulties tend to be less problematic because of the very much greater abundance of PRR particles produced.) It is possible that the surface to be sampled was dirty at the time of the exposure has become dirty since the exposure but prior to sampling or is of a nature that will produce an abundance of non-pyrotechnic material upon sampling. In these cases, gross statistical considerations and general pyrotechnic knowledge will not be sufficient to produce results with a reasonable confidence level. In such cases, and to generally increase one's confidence in the identification of suspect particles, background samples need to be taken and analyzed, and other possible sources for the suspect PRR particles need to be considered. These background samples can come from at least three different sources. They 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. They can be taken from the soil (dirt) in the local area that is expected to be free of the pyrotechnic residues of interest. If necessary, the background samples can also be taken from the primary items being sampled for PRR particles. Although not ideal, in that case, an examination of tiny angular particles that clearly appear to be non-pyrotechnic in origin can be useful in establishing the elemental signatures of non-PRR particles. Any (all) of these various background samples are useful for comparison with the suspect PRR particles.

PRR particles can be identified through the combination of spherical morphology and an elemental signature that is both consistent with being of pyrotechnic origin and inconsistent with background samples. However, it will not be possible to establish the identity and origin of each particle analyzed, and these particles must be characterized as being "indeterminate." 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 suspect particle. Further, there is no need for an exhaustive search for PRR particles. Rather, a statistical approach can be taken, in which analysis continues only until the degree of certainty reaches the level needed.

Those non-PRR particles of geologic origin, such as comprising the inorganic components of soil, can usually be eliminated from consideration based on their distinct non-spheroidal morphology. In addition, those few geologic particles that appear roughly spheroidal can almost always be eliminated based on their X-ray signatures. However, to someone without a geochemistry and pyrotechnic chemistry background, this might not be readily apparent, especially considering that, of the ten most abundant crustal elements (15), all eight of those with atomic numbers from sodium and above also appear in the list of elements potentially present in pyrotechnic compositions.

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 many EDS systems, 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 (16a). Thus, it is not uncommon to find particles that produce essentially only silicon X-rays. Further, in pyrotechnic compositions: (1) silicon is not one of the more common elements present; (2) silicon is primarily used in military formulations and in safety matches (as powdered glass); (3) silicon tends to be used only in the igniter portion of a device, which is generally only a small portion of the total amount of pyrotechnic composition in a device; and (4)

silicon is essentially always used in combination with other readily detectable elements that are present in substantial quantities in comparison to the amount of silicon. 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 virtually certain that it is of non-pyrotechnic origin, especially if particles producing similar X-ray spectra have also been found in background samples. (Note that silicates—assemblages of silicon and oxygen with other crustal elements—are commonly used in some fireworks in the form of clay plugs for tubes.) An argument, similar to that made for identifying the origin of particles primarily producing silicon X-rays, can also be made for particles exhibiting essentially only calcium X-rays, which may be one or another geologic form of calcium carbonate (16b).

Geologic particles producing combinations of X-rays are a little more problematic, but most can also be identified with a high degree of confidence. For example, feldspar refers to a group of minerals composing about 60% of the Earth's crust (16c). Most commonly, feldspars 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, most common geologic particles will have silicon or calcium as the most prevalent X-ray peak, whereas pyrotechnic material will generally have relatively little, if any, of these elements present. (For more complete information on the forensic analysis of soils using SEM/EDS, see Ref 17.)

Particles that are organic in nature (whether biologic or man-made) most generally do not have morphologies mistakable for PRR particles. Organic particles also have X-ray characteristics that greatly aid in their identification. Foremost among these characteristics is their low rate of production of X-rays with energies greater than approximately 0.6 keV. This is a result of organic particles being mostly comprised of elements with atomic numbers no higher than oxygen. Thus, while these particles still produce a bremsstrahlung continuum, it is common for biologic particles to produce no more than about one third the number of X-rays above 0.6 keV than do inorganic (geologic and PRR) particles.

While the use of approximate count rate or MCA dead time 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 constant conditions, there are a number of factors that can give rise to low count rates and dead times. As an example, for the very smallest particles (those significantly less than the interrogation depth of the electron beam) the count rate 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; however, effects such as these are expected and manageable. For the instrument and configuration used in this paper, when the dead time is less than approximately 5%, it is likely that the vast majority of the atoms in the portion of the specimen being scanned have atomic numbers less than 11.

Another useful indicator of organic particles is that the spectrum will generally not contain any peaks of major intensity in comparison with the background continuum. Usually a visual inspection of the spectrum is sufficient to reveal this; however, if desired, a quantitative measure of the peak-to-background ratio for the most prominent peak(s) in the spectrum can be produced. For the instrument and its configuration used in this paper, organic material generally produces peak-to-background ratios less than 2. As with MCA dead times, peak-to-background ratios are not a completely reliable indicator of the 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 of individual particles are reduced. Further, particles can be mixtures of organic material with other material having higher *Z* components. For example, white paper may have calcium carbonate added to make it more opaque, and other organic material may have inorganic material imbedded within or adhering to its surface.

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 to limit problems such as flaring or excessive contrast. Further, because the difference in *Z* between organic and geologic or PRR particles is not especially large, the image intensity contrast may not be sufficient to allow their differentiation.

While the majority of other inorganic (non-PRR) particles are clearly identifiable on the basis of their morphology, a few are not and deserve mentioning. Spheroidal particle morphologies are the norm for tiny bits of almost any material that was molten while airborne. Examples of this phenomenon are the particles formed during metal fabrication such as when grinding or sawing with an abrasive blade, and arc or gas welding or cutting. Another example is common fly ash. Even components of an unreacted pyrotechnic composition may meet the morphology requirements for PRR particles. For example, certain milled and atomized materials may be present that are spheroidal and in the same size range as PRR particles (see Refs 11 and 18 to 20 for more information on other sources of spheroidal non-PRR particles). Finally, components of the pyrotechnic composition that are present in excess, non-pyrotechnic materials from the device, and materials from the local environment may melt and remain as small spherical particles.

Case Example

This example comes from a case where an individual was burned when a pyrotechnic device (a consumer firework) was alleged to have exploded—sending pieces of burning composition in his direction. Figure 3 is an electron micrograph (magnification was 700×) of a small portion of one sample taken from the inside surface of the individual's clothing in the general area where the burn injury occurred. In this image, a series of six items are identified for

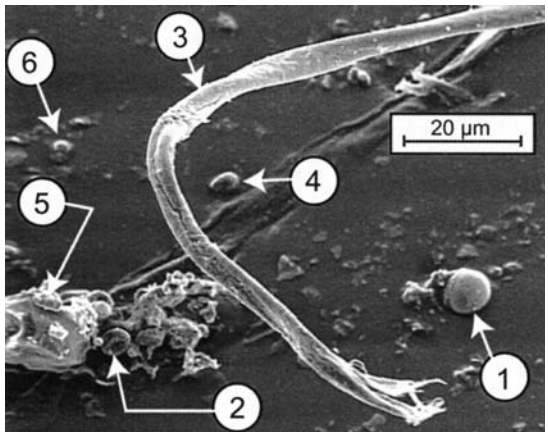

FIG. 3—*An electron micrograph identifying a series of particles (items) analyzed during an accident investigation. Items 1 and 2 are PRR particles; items 3 through 6 are various non-PRR particles. (See the text and Table 3 for details.)*

use as examples of the way the analysis was performed. (In the actual investigation many other particles from other portions of this and other samples were also analyzed.) Figure 4 is a collection of the X-ray spectra, two from laboratory work plus those collected from the six particles (items) identified in Fig. 3. The uppermost X-ray spectrum is the gross spectrum of one of the unreacted compositions taken from the type of firework suspected to have been responsible for the injury. (This firework contained four different pyrotechnic compositions, which would normally burn in sequence one after the other.) Immediately below that is a spectrum typical of a PRR particle produced by burning this same pyrotechnic composition under laboratory conditions.

Table 3 presents the results from the analysis of the six particles identified in Fig. 3 and illustrates a typical methodology used in performing an analysis of PRR particles. (The categories and classifications will often need to be 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. (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 to the indeterminate category.

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. 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 to the indeterminate category.

Particles 1 and 2 have the correct morphology for a PRR particle and produced reasonably high X-ray count rates. Their chemistry is consistent with that of a PRR particle that had been confirmed through the production of effectively identical (matching) PRR particles in the laboratory using one of the suspect pyrotechnic compositions. Further, many more particles with the same morphology and elemental signature were found distributed on clothing in the general area where the injury occurred, specifically on both the inside and outside surfaces of remnants of the individuals outer and underclothing. Since no similar particles were found on background areas of clothing remote from the area of the injury, Particles 1 and 2 are identified as PRR particles.

Item 3 has the obvious appearance of a fiber, most likely from the individual's clothing itself. Its counting dead time and peak-to-background ratio are quite low, suggesting it consists mostly of low *Z* atoms. Its chemistry is essentially devoid of those major elements associated with geologic or pyrotechnic materials. Accordingly, 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 to improve image quality for publication.) Particle 4 is roughly spheroidal, although it is elongated with a fairly pointed end and 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) 3, it has been conservatively

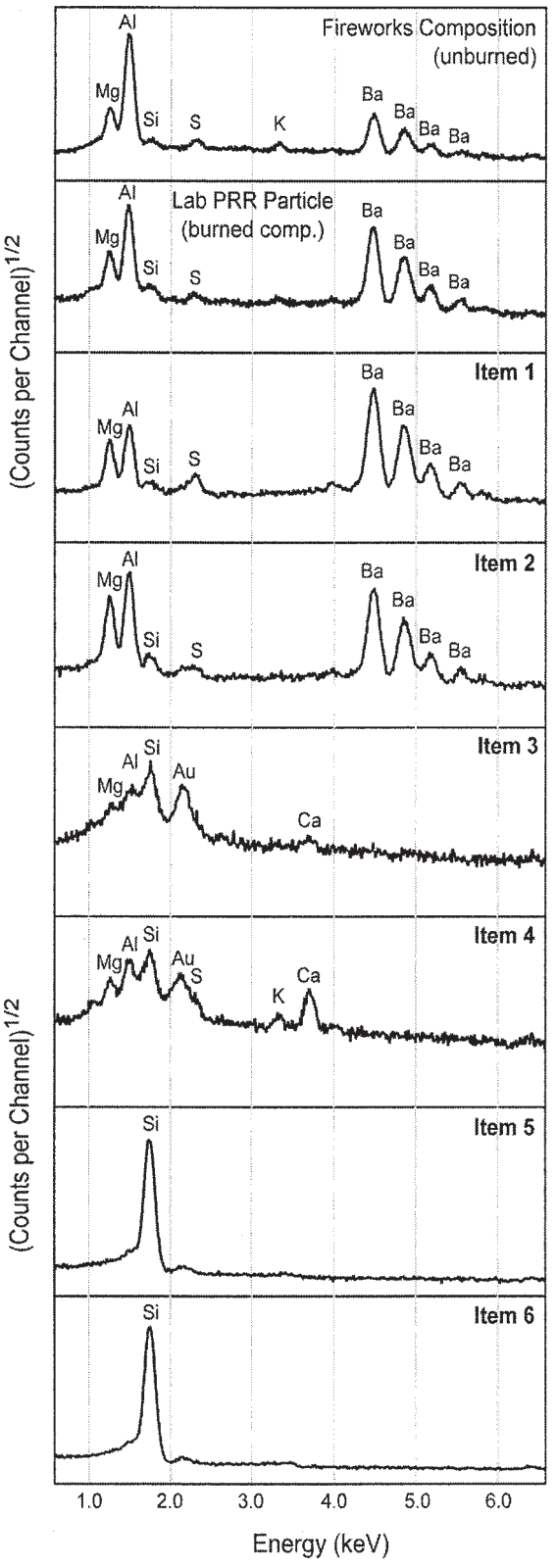

FIG. 4—*X-ray spectra collected from the unreacted fireworks composition, laboratory produced (known) PRR particle, and the six particles (items) identified in Fig. 3.*

TABLE 3—*Analytical results for the particles identified in Fig. 3.*

Particle Number	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	13.0	Geologic	Geologic
6	Spheroidal	14	16.0	Geologic	Geologic

designated as indeterminate because of the somewhat increased prominence of X-ray peaks often 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 5 is of non-spheroidal morphology, has a relatively high dead time, has a very high peak-to-background ratio, and exhibits chemistry consistent with being silica sand and quite inconsistent with being of pyrotechnic origin. 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. With a high degree of confidence, Particle 5 is identified as being of geologic origin. Except for its spheroidal shape, Particle 6 is like that of Particle 5. Geologic particles that have been mobile in the environment for a prolonged time tend to become nearly spherical in shape. Accordingly, with a high degree of confidence, Particle 6 is also identified as being of geologic origin.

Most of the particles cataloged in this example were not PRR particles. During an analysis 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 so as to reasonably represent the range of different non-PRR particles found, with most of the time 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 identify and analyze PRR particles in the course of investigating incidents involving pyrotechnic materials can provide information with a degree of sensitivity and specificity that is unavailable with other commonly used techniques. The degree of confidence in the results will vary greatly depending on things such as the elemental and physical nature of the particles, their abundance and distribution within the area of the incident, their degree of rarity in background samples, and the extent to which there are possible alternative sources or explanations.

Given the widespread 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 incidents involving pyrotechnics. Obviously one reason for its infrequent use is that many investigations would not benefit greatly from the type of information that could be developed. However, even for those incidents where PRR particle analysis would be of significant benefit, often that analysis is not performed. After speaking with several investigators, the authors have concluded the likely reason for its under-use is simply that many investigators are not sufficiently aware of the PRR particle analysis methodology and the information it can provide.

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