

Characterization of Pyrotechnic Reaction Residue Particles by SEM / EDS

K. L. and B. J. Kosanke

PyroLabs, Inc., 1775 Blair Rd., Whitewater, CO 81527, USA

and

Richard C. Dujay

Mesa State College, Electron Microscopy Facility, Grand Junction, CO 81501, USA

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). In recent years, this same methodology is beginning to find use in detecting and characterizing pyrotechnic reaction residue particles (PRRP) 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 PRRP are identified by their morphology (typically 1 to 20 micron spheroidal particles) using a SEM and then analyzed for the elements they contain using X-ray EDS. This can help to identify the general type of pyrotechnic composition involved. Further, more extensive laboratory comparisons can be made using various known pyrotechnic formulations.

Keywords: pyrotechnic reaction residue particle, PRRP, gunshot residue, GSR, scanning electron microscopy, SEM, energy dispersive spectroscopy, EDS, morphology, X-ray elemental analysis

Introduction

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 the size from approximately 0.5 to 5 microns, and principally originate from the primer composition. 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 (gun) 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, much of which have physical characteristics similar to GSR and can be detected and analyzed using much the same 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 also applies to the identification of pyrotechnic reaction residue particles (PRRP). However, there are three important differences. First, the chemical elements present in PRRP are mostly different and often more varied than those most commonly found in GSR. Second, many of the elements that are present in pyrotechnic residues are also found in other (non-pyrotechnic) materials. Third, the quantity of PRRP produced during an event is generally

several orders of magnitude greater than that for GSR.

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 PRRP, relatively little information regarding its use for PRRP analysis has appeared in the literature. Most of the articles are recent and in the context of PRRP that may be found to meet the criteria of GSR.^[5-9] The primary exceptions known to the authors are: an article produced at the Forensic Explosives Laboratory in the United Kingdom;^[10] three earlier introductory articles by the authors of this article, written for researchers with varying degrees of knowledge of pyrotechnics, GSR analysis and SEM / EDS techniques;^[11-13] and a compilation of data on the PRRP produced by consumer fireworks.^[14] The scarcity of published information about PRRP analysis is unfortunate, because for those occasional cases potentially involving pyrotechnic residues, this can be an especially useful investigative tool about which too few forensic analysts are aware.

SEM / EDS Equipment Used

Most of what is described in the remainder of this article is independent of the type of instrument used. However, it may be useful to describe the instrument most often used by the authors. The SEM is a manually operated AMRAY 1000, recently remanufactured by E. Fjeld Co.^[15] For this work, the instrument is most often used with an accelerating potential of 20 kV and operated in the secondary electron mode. The instrument provides software driven digital imaging. The X-ray spectrometer is energy dispersive, using a KeveX Si(Li) detector^[16] (with a beryllium window) in conjunction with an American Nuclear System^[17] model MCA 4000 multichannel analyzer using their Quantum-X software (version 03.80.20). 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 article, some specimens were lightly sputter coated with gold.) Finally, it should be noted that additional and more detailed information on the techniques used by the

authors in PRRP collection and analysis will be included in a subsequent article.

In the spectra reproduced for this article, the vertical scales were normalized such that the largest X-ray peak in each spectrum has the same, full-scale height. 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. Similarly, the portion of the spectrum below approximately 0.5 keV was not included. This was done to more clearly display the spectral regions of interest for this article.

Pyrotechnic Reaction Residue Particles (PRRP)

Morphology

In essentially every case, pyrotechnic reactions produce sufficient thermal energy to produce molten reaction products. Further, 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 one micron, with those in the range from about 1 to 20 microns most often chosen for analysis. 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 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 PRRP that were molten while airborne to become spherical (or at least spheroidal) in shape. The collection of electron micrographs in Figure 1 demonstrates the appearance of some PRRP. In this case, the particles are in the range of approximately 5 to 20 microns in diameter.

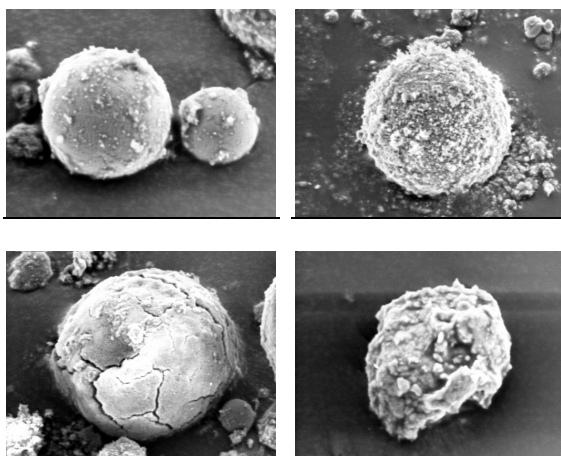


Figure 1. A range of typical 5 to 20 micron spheroidal pyrotechnic reaction residue particles (PRRP).

In examining GSR, it is apparently somewhat common to find multiple particles having agglomerated into grape-like clusters.^[18] In the authors' experience, except for agglomerations of the type seen in Figure 1 (tiny particles collecting on the surface of larger ones, and poorly formed composites as the lower right image), such orderly agglomerations have not been observed for PRRP.

Although the fraction of PRRP to non-PRRP is much higher than is found when doing GSR work, often it is still quite low. Accordingly, as with GSR, it is appropriate to use morphology as an aid in selecting particles for further analysis. (This subject is discussed in somewhat greater detail in reference 11.) Although not specifically discussed in this article, note that PRRP can fail to be deposited and can be lost or transferred for many of the same reasons and in much the same way as with GSR particles.

Before leaving the subject of PRRP morphology, it is important to mention that, while in essentially every instance some spherical particles will be produced during pyrotechnic reactions, it is possible that much of the pyrotechnic residue produced will collect as a once molten slag. This is particularly true for slow burning compositions, compositions that do not form gaseous reaction products, and especially when those reactions occur within an unexploded container of some sort. (To help emphasize that not all pyrotechnic reaction residues will be in the

form of particles, this article has adopted the formalism of referring to them as pyrotechnic reaction residue *particles* (PRRP) a sub-category of the total pyrotechnic reaction residues produced. In cases where pyrotechnic reaction slag is present, collecting and analyzing that slag using conventional chemistry may provide the best information about the nature of the unreacted pyrotechnic composition. However, even in such cases, the collection and analysis of PRRP can aid in identifying items and persons present in the immediate area at the time of the incident. Further, while beyond the scope of this article, a careful analysis of the distribution of such PRRP may allow one to determine details of the nature and course of an incident that are not available using other means.^[19]

X-ray Signatures

Table 1 is a list of chemical elements somewhat commonly found in pyrotechnic compositions. Included in the table is an attempt to estimate the relative overall frequency of each chemical element's presence in civilian and/or military compositions. 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. Note that while lead, barium and antimony compounds are used in pyrotechnics, their use is not particularly common and only very rarely, if ever, are all three present in the same pyrotechnic composition.^[5,9] Further, even when some combination of lead, barium and antimony are present in PRRP, typically much lower atomic number elements predominate in those PRRP. Accordingly, unlike when working with GSR particles, one cannot rely on there being significant backscatter electron brightness contrasts of PRRP to facilitate locating them. For this reason (and the relatively low sensitiveness to backscattered electrons of the instrument used by the authors) most commonly the instrument is operated in the secondary electron mode.

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

Element ^(a)	F/P ^(b)	Element ^(a)	F/P ^(b)
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		

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

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 expressed in the solid residues to the same degree that they were in the unreacted composition. For example, permanent gases produced in the reaction will be lost. To the contrary, in a few cases, minor components may become concentrated in PRRP, because of their separation from other components as a result of the pyrotechnic reaction.^[20]

In Figure 2, the three upper X-ray spectra (1 to 3) are from individual particles in an unreacted firework flash powder with the formulation: 60% potassium perchlorate, 30% magnesium-aluminum alloy 50:50 (commonly called magalium), 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 somewhat

representative of the average composition of the unreacted flash powder. (Through the use of the term “gross” rather than “bulk” it is hoped to avoid implying a high level of accuracy in the element ratios of the sample.) X-ray spectrum 5 is typical of those produced by PRRP in the range of 5 to 20 microns resulting from this flash powder composition. In spectra 4 and 5, note the

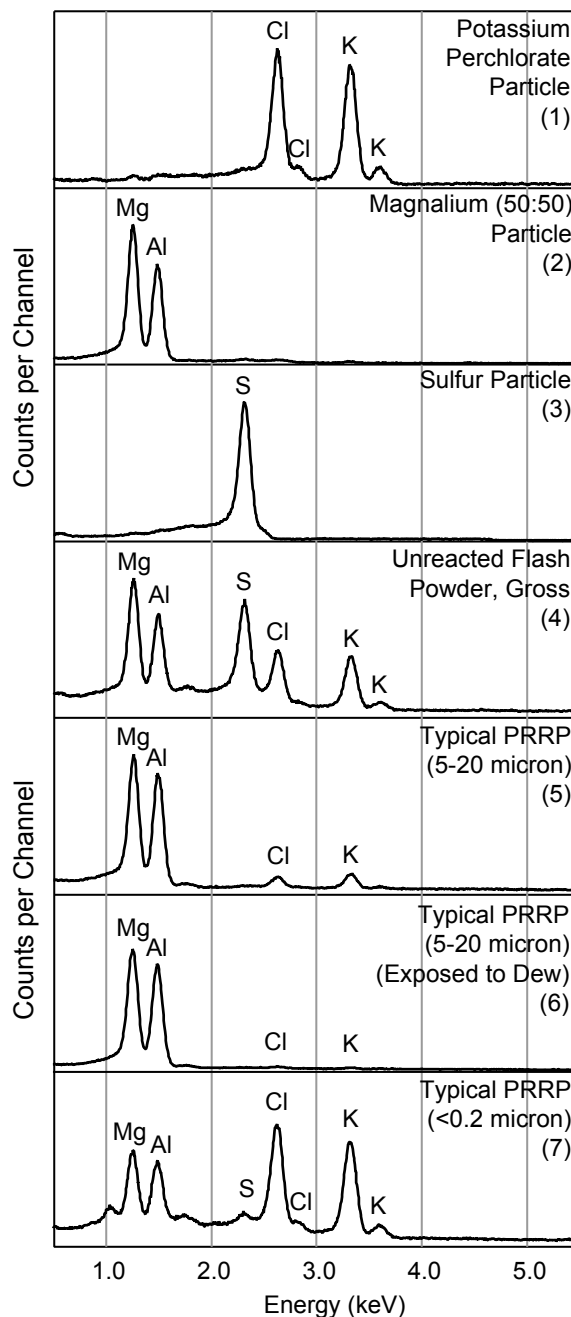


Figure 2. X-ray spectra associated with a pyrotechnic flash powder.

difference in the sulfur peaks; while quite prominent in the unreacted gross spectrum (4), it is missing from the typical PRRP 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 PRRP. (It should not be assumed that there will always be similar reductions in the presence of sulfur peaks for other pyrotechnic compositions. In some cases, sulfur reacts to form sulfates and sulfides that remain in the residues. A prime example of where sulfur persists to some extent in PRRP is in the case of Black Powder.)

The reduction of the potassium and chlorine peaks between spectra 4 and 5 is a little more complicated to explain, but it demonstrates some of the thinking needed to properly interpret PRRP results. In this case, the reduction is the result of differences in the physical properties of the condensing reaction products. A somewhat simplified chemical equation for the pyrotechnic reaction of this flash powder is

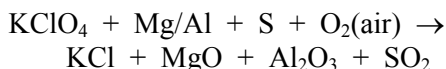


Table 2 lists the melting and boiling points of the products of this reaction. Based on thermochemical modeling calculations, all of these reaction products will initially be vaporized at the completion of the reaction.^[21] As the vapor cloud expands after the explosion, it quickly cools and the metal oxides condense, then solidify. Because of potassium chloride's lower boiling point, 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 only been deposited on the surface of the metal oxide PRRP. This is readily confirmed by exposing the particles to moisture, which dissolves the highly soluble potassium chloride from the surfaces, to leave the insoluble metal oxide cores. The ease and extent to which moisture acts to remove potassium chloride can be seen by examining spectra 5 and 6 in Figure 2. The difference between these spectra is that the particle in spectrum 6 has been exposed to moderate dew, which was sufficient to wash essentially all of the potassium chloride from the PRRP.

Table 2. Flash Powder Reaction Products
[22,23]

Reaction Product	Temperature (°C)	
	Melting	Boiling
KCl	771	1478 ^(a)
MgO ^(b)	2832	3260
Al ₂ O ₃ ^(b)	2054	3528
SO ₂	-73	-10
K ₂ SO ₄ ^(c)	1069	1689

- Note that while KCl has a reported melting point, its vaporization is nonetheless characterized in some reference texts as subliming rather than boiling.^[22]
- For simplicity, MgO and Al₂O₃ are listed as the reaction products; however, analysis by X-ray diffraction indicates that some of the crystallized reaction product is actually MgAl₂O₄, which has a melting point of 2135°C.^[22]
- K₂SO₄ is a potential reaction product that might be formed and collect with KCl in the smaller PRRP and may account for the weak sulfur peak in spectrum 7.

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 Figure 2. It is reasoned that, because the larger PRRP tend to remain hot longer, the potassium chloride is predominantly found to be associated with the smallest particles. This can readily be seen in a comparison of spectra 5 and 7 in Figure 2, where spectrum 7 is typical of particles that are less than 0.2 microns in diameter. The small sulfur peak seen in spectrum 7 is thought to be contributed by the conductive carbon dot used to secure the sample. The less than 0.2 micron particles are sufficiently tiny so as to allow the electron beam to stimulate X-ray emissions from the underlying carbon dot (which has previously been found to produce a weak sulfur peak). However, it must be acknowledged that it is possible that a small fraction of sulfur in the pyrotechnic reaction was oxidized to potassium sulfate, and because of its comparatively low boiling point, it also became concentrated in the smaller PRRP.

In addition to the variability that can exist in the chemistry of PRRP 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 generally are on the order of 10 to 20 percent and are thought to reflect such things as 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 made more difficult to observe because of rather large random variations in PRRP chemistry due to the lack of complete chemical equilibrium in the reactions occurring in the expanding cloud of reaction products. 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 percent. (Recall that the magnesium and aluminum is 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 PRRP 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 are such that a large degree of variability from one PRRP to the next must be expected. However, to the contrary, the distribution of elements across the surface of individual PRRP seems to be quite uniform. (Unfortunately, a more complete discussion of these phenomena is beyond the scope of the present article.)

Particle Identification

It is not intended that the information included in this section be all inclusive, especially in regard to non-PRRP. There is a vast amount of that information available from many different sources (a few of which are referenced below). Only enough material has been included to make this introductory article reasonably complete.

Pyrotechnic Reaction Residue Particles (PRRP)

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, samples taken from those locations will

contain a high proportion of PRRP. This combined with the relatively small number of non-PRRP that fit the morphology criteria for residues, often allows the tentative identification of residue particles based primarily on morphology and statistical considerations alone. For example, consider the case of examining a sample collected from such a PRRP rich item. Of the first 50 suspect particles selected (because they meet the PRRP 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 quite likely that the 45 particles are from the pyrotechnic event being investigated. (One's level of confidence increases if the X-ray elemental signature for those 45 particles is not found to be associated with any background source.)

More commonly, the exposure to pyrotechnic residues is more limited, either in the duration of exposure, by the distance from the event, or both. In addition, there are all of the potential difficulties associated with the recovery of GSR. Further, 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 upon sampling. In these cases, gross statistical considerations and general pyrotechnic knowledge will not be sufficient to produce results with a high 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 PRRP 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. (How far away is sufficient, will depend on things such as the size and explosivity of the event.) Background samples can be taken of the soil (dirt) in the local area that is thought to be reasonably free of the pyrotechnic residues of interest. Finally, if necessary, background samples can also be taken from the primary items being sampled for PRRP. Although not ideal, in that case, an examination of angular particles

that clearly appear to be non-pyrotechnic in origin can be useful in establishing the elemental signatures of non-PRRP. Any (all) of these various background samples are useful in comparing with the suspect PRRP.

Accordingly PRRP can be identified through the combination of spherical morphology, particle size, and an elemental signature that is both consistent with being of pyrotechnic origin and substantially absent in background samples. Typically, it will not be possible to establish the identity and origin of each particle analyzed and these must be characterized as being “indeterminate”. However, in most cases the sheer number of PRRP 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 the search for PRRP to be exhaustive. Rather a statistical approach can be taken, in which analysis continues only until the degree of certitude reaches the level needed.

Geologic Particles

For the most part, those non-PRRP of geologic origin, such as comprising the inorganic components of soil, can 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 after considering that, of the ten most abundant crustal elements,^[24] 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 PRRP is knowledge of the likely elemental signatures for both types of particles. For example, for many common EDS systems, the most abundant geologic element that can be detected is silicon, and the most common minerals are one or another form of quartz (silicon dioxide) and various silicates.^[25a] Accordingly, it is not uncommon to find particles that produce essentially only or primarily silicon X-rays. Further, it is known in pyrotechnic compositions that: 1) silicon is not one of the more common

elements found; 2) silicon is primarily used in military formulations and in safety matches (as powdered glass); 3) silicon tends to be only used in the igniter portion of a device, which is generally only a small portion of the total amount of pyrotechnic composition; and 4) silicon is essentially always used in combination with other readily detectable elements that are present in substantial quantities. Thus, when a particle is examined and found to exhibit only or primarily silicon X-rays, even when it has a morphology roughly consistent with PRRP, 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, as clay, in the form of plugs for tubes are commonly used in some fireworks.) An argument similar to that made for particles producing primarily silicon X-rays can be made for particles exhibiting primarily calcium X-rays, which may be one or another geologic form of calcium carbonate and other minerals.^[25b]

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 making up about 60% of the Earth's crust.^[25c] 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 PRRP. 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 present. (For more complete information on the forensic analysis of soils using SEM / EDS, see reference 26.)

Organic Particles

Like particles of geologic origin, those that are organic in nature (whether biologic or man-made), generally do not have morphologies mistakable for PRRP. Also, similar to geologic particles, organic particles have X-ray characteristics that aid greatly 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 1/3 the number of X-rays above 0.6 keV that inorganic (geologic particles and PRRP) produce.

While the use of approximate 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 dead-times. For 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 article when the dead time is less than approximately five 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 (sodium).

Another useful indicator of organic particles is that the spectrum will generally not contain any peaks of major intensity in comparison with the background (Bremsstrahlung) 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 article, purely 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 prevalent atomic number. When there is a mixture of several moderate to high atomic number (*Z*) materials in the particle, such that there are many prominent peaks in the spectrum, peak-to-background ratios are reduced. Further, sometimes particles are mixtures of organic material with other material having higher atomic number (*Z*) components. For example, white paper has calcium carbonate added to make it whiter and more opaque, and other or-

ganic material may similarly have inorganic material imbedded within or adhering to its surface.

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

Other Inorganic Particles

While the majority of other inorganic 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 most any material that was molten while airborne. One example of this phenomenon is the particles formed during metal fabrication such as grinding (including “chop sawing”) and arc or gas welding or cutting. Other examples are common fly ash and even components of an unreacted pyrotechnic composition, wherein certain milled and atomized materials are included that are spheroidal and in the same size range as PRRP. (See references 11, and 27 to 29 for more information on other sources of spheroidal non-PRRP.)

Case Example

This example comes from a case wherein 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 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. (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 investigation, 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 4 is a collection of

the X-ray spectra, two from laboratory work plus those collected from the six particles (items) identified in Figure 3.

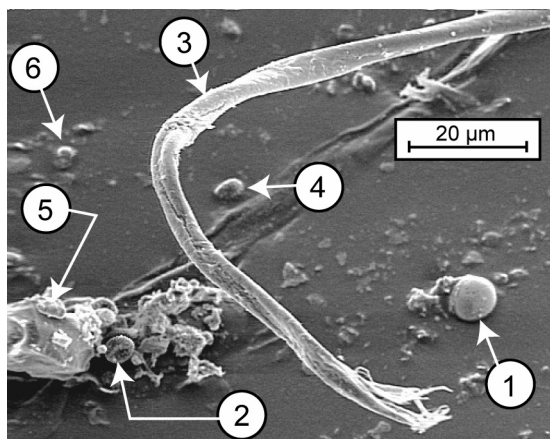


Figure 3. An electron micrograph identifying a series of particles (items) analyzed during an accident investigation. (See Table 3.)

The uppermost X-ray spectrum is the gross spectrum of one of the four different unreacted compositions taken from the type of firework suspected to have been responsible for the injury. Below that is a spectrum typical of a PRRP produced by burning this same pyrotechnic composition under laboratory conditions.

Table 3 presents the results from the analysis of the six particles identified in Figure 3 and illustrates a typical methodology used in performing an analysis of PRRP. However, the categories and classifications will often need to be adjusted for specific investigations and generally will not be formalized by the use of a table to classify the individual particles. 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 man-made) often have this appearance, while PRRP 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*.

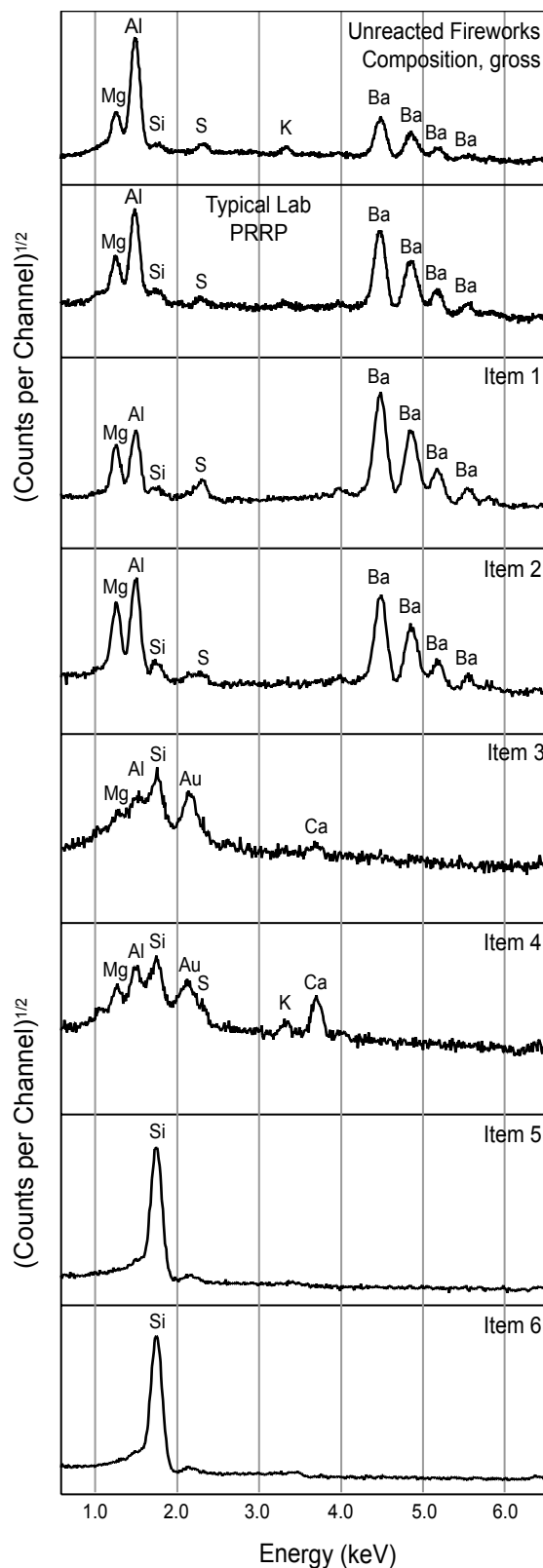


Figure 4. X-ray spectra from laboratory samples and the six particles identified in Figure 3.

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

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

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 being PRRP, which had been confirmed through the production of effectively identical (matching) PRRP 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. Finally, no similar particles were found on background areas of clothing remote from the area of the injury. Accordingly, particles one and two are identified as PRRP.

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. The same gold X-rays were produced by all of the particles being analyzed; however, when the particle being examined produces 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 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-PRRP*.

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 PRRP, 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 period of 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 PRRP. As a practical matter, during an analysis it would be unusual to bother to document the nature of a high percentage of non-PRRP. Typically, only enough of these particles would be analyzed and documented such as to reasonably represent the range of different non-PRRP found. Instead, most of the time would be devoted to finding and analyzing PRRP. 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 PRRP 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. That is not to say these analyses are necessarily easy and without potential pitfalls. 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 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 incidents involving pyrotechnics. Obviously one reason for its infrequent use is that many investigations would benefit relatively little from the type of information that could be developed. However, even for those incidents where PRRP analysis would be of significant benefit, often that analysis is not performed. After speaking with several investigators, the authors have con-

cluded the likely reason for its under use is simply that many investigators are not sufficiently aware of the PRRP analysis methodology and the information it can provide. Therein lies the purpose of this introductory article, to disseminate some basic information about PRRP analysis to the forensic community.

In further support of the goal of disseminating information regarding PRRP identification and analysis, one additional article has recently been published and at least two more are planned. The already published article^[19] further demonstrates the nature and utility of the information produced by considering a series of investigations of actual and staged incidents. The planned articles will present much more information about the mechanics of specimen production, collection, and their subsequent analyses, and an investigation of some of the complexities of the chemistry of pyrotechnic reactions and PRRP.

Acknowledgments

The authors are grateful to J. McVicar, J. Gicalone, and M. Trimpe for providing technical comments on an earlier draft of this paper.

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) H. H. Meng and B. Caddy, "Gunshot Residue Analysis—A Review", *Journal of Forensic Science*, Vol. 42, No. 4, 1997, pp 553–570.
- 4) *The Illustrated Dictionary of Pyrotechnics*, Journal of Pyrotechnics, 1996.
- 5) 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.

- 6) 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.
- 7) 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.
- 8) J. R. Giacalone, "Forensic Particle Analysis of Microtrace Pyrotechnic Residue", *Scanning*, Vol. 21, No. 2, 1999, pp 100–101.
- 9) M. Trimpe, "Analysis of Fireworks for Particles of the type Found in Gunshot (GSR)", abstract only, AAFS Meeting, Seattle, 2001.
- 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*. also in *Science and Justice*, Vol. 41, 2001, pp 73–80.
- 11) K. L. & B. J. Ksanke and R. C. Dujay, "Pyrotechnic Reaction Residue Particle Identification by SEM / EDS", *Journal of Pyrotechnics*, No. 13, 2001, pp 40–53; also in *Selected Pyrotechnic Publications of K. L. and B. J. Ksanke, Part 6 (2001 and 2002)*, Journal of Pyrotechnics, 2005.
- 12) K. L. Ksanke and R.C. Dujay, "Forensic Identification of Pyrotechnic Reaction Particles", *Microscopy Today*, No. 01-7, 2001.
- 13) K. L. & B. J. Ksanke and R.C. Dujay, "Identification of Pyrotechnic Reaction Residue Particles", *International Association of MicroAnalysts Newsletter*, Vol. 3, No. 2, 2002.
- 14) M. Trimpe, Hamilton County Coroners Office, 3159 Eden Ave., Cincinnati, OH 45219.
- 15) E. Fjeld Co., N. Billerica, MA, USA.
- 16) Kevex, Inc. Foster City, CA, USA.
- 17) American Nuclear Systems, Inc., Oak Ridge, TN, USA.
- 18) M. J. McVicar, private communication (2001).
- 19) K. L. Ksanke, R.C. Dujay, and B. J. Ksanke, "Pyrotechnic Reaction Residue Particle Analysis", *Journal of Forensic Sciences*, Vol. 51, No. 2, 2006.
- 20) J. Giacalone, private communication (2001).
- 21) W. Meyerriecks, private communication of thermodynamic modeling results using his CEQ code (2000).
- 22) *CRC Handbook of Chemistry and Physics*, 75 ed., CRC Press, 1995.
- 23) The ICT Thermodynamics Code Users Manual, Institut Chemische Technologie, 2005.
- 24) D. L. Holmes, *Holmes Principles of Physical Geology*, John Wiley, 1978, p 46.
- 25) *Van Nostrand's Scientific Encyclopedia*, 5th ed., Van Nostrand-Reinhold, 1976; [a] p 1857; [b] p 400; [c] p 1012.
- 26) 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.
- 27) K. L. & B. J. Ksanke and R. C. Dujay, "Pyrotechnic Particle Morphologies—Metal Fuels", *Journal of Pyrotechnics*, No. 11, 2000, pp 46–52; also in *Selected Pyrotechnic Publications of K. L. and B. J. Ksanke, Part 6 (2001 and 2002)*, Journal of Pyrotechnics, 2005.
- 28) K. L. & B. J. Ksanke and R. C. Dujay, "Pyrotechnic Particle Morphologies—Low Melting Point Oxidizers", *Journal of Pyrotechnics*, No. 12, 2000, pp 5–15; also in *Selected Pyrotechnic Publications of K. L. and B. J. Ksanke, Part 6 (2001 and 2002)*, Journal of Pyrotechnics, 2005.
- 29) W. C. McCrone et al, *The Particle Atlas: An Encyclopedia of Techniques for Small Particle Identification*, Ann Arbor Science Publication, 1973.