Analysis of Pyrotechnic Components

Results of chemical, thermal and mechanical insult testing of components of four fireworks samples
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List of Acronyms

ABL - Alleghany Ballistics Laboratory
ATF - Bureau of Alcohol, Tobacco, Firearms and Explosives
ATF-FTIR - Attenuated total reflectance Fourier-transform infrared spectrometry
ARA - Applied Research Associates
CSB - U.S. Chemical Safety Board
DI - deionized water
DSC - differential scanning calorimetry
EDS - electrostatic discharge
EDAX - energy dispersive X-ray spectrometry
FTIR - Fourier-transform infrared spectrometry
IC - ion chromatography
ICP-AES - inductively coupled plasma atomic emission spectrometry
LC/MS - liquid chromatography mass spectrometry
MBOM - modified Bureau of Mines
ml - milliliter
MIL-STD - military standard
NA - not applicable
NCOI - non-conflict of interest
PETN - pentaerythritol tetranitrate
PPE - personal protective equipment
RDX - cyclotrimethylenetrinitramine
SEM - scanning electron microscopy
TIL- threshold of initiation level

1.0 Executive Summary

This document describes testing of the physical and chemical characteristics of component samples of four fireworks collected and provided by the CSB to determine whether these samples had chemical or physical characteristics that would potentially increase their susceptibility to unintentional or accidental initiation. This document contains a narrative that discusses the merged results of an extensive set of mechanical insult, thermal sensitivity and chemical composition testing. All the raw analytical data is present in the attached Appendices.

Although no formal testing protocol exists to determine sensitivity of pyrotechnic materials, all analyses were performed with well-characterized, industry standard testing. Sensitivity to mechanical insult was evaluated through use of calibrated instruments and military-approved methods to establish response to impact, friction and electrostatic discharge. These mechanical insult tests showed that although some of the materials were indeed very sensitive, that appreciable similarity exists between samples of material having the same purpose within the firework (the components are discussed in the next section). It should also be noted at the outset that these materials are expected to be quite sensitive, and that our results are in agreement with the basic nature of all fireworks materials, especially flash powder mixtures.

Elemental composition analysis was performed on the dry samples with scanning electron microscopy and x-ray elemental analysis (SEM-EDAX) and after partial dissolution in water, by inductively-coupled plasma spectrometry (ICP-AES). Anions were analyzed with liquid chromatography/mass spectrometry (LC/MS) (perchlorate) and ion chromatography (IC) (anions, in this case, chlorate and nitrate), and also by attenuated total reflectance Fourier-transform infrared spectrometry (ATF-FTIR) analyses. The results of the chemical analysis demonstrated no definitive unusual chemistry in any of the samples, and that the composition of different samples having the same purpose within the fireworks was relatively conserved.

The likelihood of adverse reaction when exposed to high temperatures was evaluated with differential scanning calorimetry. None of the samples exhibited sensitivity to temperatures less than 350 °C.

Key findings of the testing:

- The presence of sensitizing chlorates was not established.
- Thermal and testing regarding susceptibility to mechanical insult indicate that the flash powder type components are in general quite sensitive relative to standard reference material (military explosives and lab-generated flash powder), but that this sensitivity was expected by virtue of the chemical composition of the materials.

2.0 Introduction

Fireworks are a class of explosive pyrotechnic devices used for aesthetic, cultural, and religious purposes. They are most commonly used as part of a fireworks display. Fireworks produce four primary effects: noise, light, smoke and floating materials (confetti, for example). They are designed to burn with flames and sparks of many colors. Displays are popular throughout the world and are the focal point of many cultural and religious celebrations, including Independence Day in the U.S.

Fireworks are generally classified as to where they perform, either as a ground or aerial firework. In the latter case they may provide their own propulsion (typically called a skyrocket) or be shot into the air by a mortar (aerial shell). The most common feature of fireworks is a paper or cardboard tube or casing filled with the combustible material, often pyrotechnic stars. The aerial shell is the backbone of today's commercial aerial display. A smaller version for consumer use is known as the festival ball in the United States. There are also ground fireworks; while less popular than aerial fireworks, they can produce various shapes like rotating circles, stars and 3D globes.

Fireworks are composed of several types of materials that vary with their purpose in the overall device. Figure 1 shows the energetic material components of typical commercially-produced aerial display fireworks, consisting of an ignition fuse, lifting charge, time fuse, bursting charge and pyrotechnic “stars” or “comets.” These components, shown in Figure 1, each contain specific types of materials that enable that component to perform its established purpose.[1]

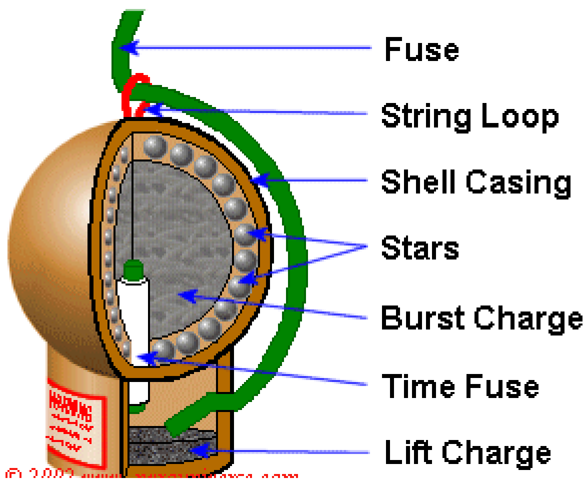


Figure 1 Components of a typical aerial firework[1]

Although there are numerous variations of actual fireworks construction, the lift and burst charges are propellants usually very similar to black powder (i.e. gun powder), comprised of mixtures of potassium nitrate (KNO_3), charcoal and sulfur. Upon ignition, these materials generate the large quantities of gas needed to propel the rest of the device into the air.

Flash powders, so named because of their initial use in early flash photography, are often used in fireworks to create a loud report and have compositions consisting of mixtures of potassium perchlorate, aluminum and magnesium powders and sulfur. The flash powder itself is often in the form of a very fine, silvery-colored powder, and in this powder form will react very quickly, especially when contained, to generate intense noises and brief, bright flash effects.

The stars or comets are formed by blending variations of flash powder with binders so that they can be pressed or extruded into consolidated pellets. In pellet form, the stars or comets will burn relatively slowly to produce the aerial showers so popular in fireworks displays. Based on the literature, there are many types of stars and comets. A couple of well-represented recipes from Skylighter.com are shown here. The first type consists of a perchlorate/nitrate/gum rubber base which contains potassium perchlorate, a mix of finely divided aluminum and magnesium powders, very fine charcoal powder, potassium nitrate, red gum, and powdered sulfur. In another major type, potassium perchlorate is substituted with potassium nitrate and blended with the fine charcoal powder, sulfur, dextrin, and flaked aluminum.[2]

Metal salts are added to create the colors associated with the fireworks. For example, strontium nitrate yields a bright red color, sodium nitrate is yellow and copper salts yield both blue and green, depending upon the anion associated with the copper.

These components are assembled into a device as shown in Figure 1, and launched from a mortar to begin the processes that result in the display. As previously described, the lift charge propels the shell out of the mortar tube, and the time fuse ignites the burst charge at the correct altitude. The burst charge than creates the explosion of the shell and the release and ignition of the stars, causing the pattern that appears in the sky.

One primary aim of the work was to test all the materials for the presence of chlorates, which used to be a common ingredient in flash powder mixtures. These compounds are recognized by the community to yield even more sensitive flash powder mixes than the more commonly used perchlorates. Chlorates are more dangerous in several ways. Firstly, they are known to be more inherently sensitive to mechanical insult. In addition, chlorates can react with sulfuric acid to form a highly reactive solution of chloric acid and potassium sulfate:

$$2\ KClO_3 + H_2SO_4 \rightarrow 2\ HClO_3 + K_2SO_4$$

The products of the above reaction are sufficiently reactive that they will spontaneously ignite if combustible material (sugar, paper, etc.) is present.[3] This is a particular problem when sulfur is present in the mixture, as almost all sulfur components will yield small amounts of sulfuric acid with time and exposure to humidity. The presence of chlorate compounds in fireworks is no longer common, but testing for this anion is important because of the additional danger in handling they represent.

The results discussed in this report all indicate that the material submitted to us for testing is within the range of ordinary pyrotechnics recipes that can be discovered in literature and on the internet. This is not to say that the materials are not sensitive; they certainly are, as shown by the testing related to exposure to calibrated impact, frictional forces and electrostatic discharge. Quotations in the text describe that this degree of sensitivity is to be expected.

3.0 Approach and Objectives

ARA received samples of 4 fireworks, each separated into subsamples by pyrotechnic component. These samples were chosen for analysis to determine if they were more sensitive to initiation than expected. This testing includes susceptibility to reaction by exposure to impact, frictional forces and exposure to electrostatic discharge, as well as chemical and thermal analysis. Altogether, 16 sampled materials were subjected to testing, along with five standard materials. Descriptions of all these materials are presented in Table 1.

Table 1. Samples and standards analyzed during this program

Name of sample	Physical Description	Label markings	Amount delivered
O-Triple C #A	fine gray sparkly powder		5.157 g
O-Triple C #B	small black pebbles		8.294 g
O-Triple C #C	round silver/gray balls about 0.25” in diameter		10.241 g
Sky Festival #A	large gray pellets w/ black & brown crumbs	“sm”	2.473 g
Sky Festival #B	large gray pellets w/ black & brown crumbs		2.482 g
Sky Festival #C	fine gray sparkly powder	“Lrg”	4.679 g
Sky Festival #D	fine gray sparkly powder	“lrg tube”	5.063 g
Sky Festival #E	black particles, about 0 .5 mm across with copper colored dust	“Large tube lift charge”	1.818 g
Sky Festival #F	copper-colored powder with black particles	“Small ‘comet’ tube Lift Charge”	0.714 g
Sky Festival #G	grayish coarse powder	“Small ‘Comet’ Tube Lift Charge Sample”	1.858 g
Halawa #A	small black pebbles	“Lift charge”	6.680 g
Halawa #B	fine gray powder, with larger chunks		5.656 g
Halawa #C	fine gray powder		5.706 g
Krazy Kids #A	small black pebbles	“Lift, 2 charges BSP”	8.178 g
Krazy Kids #B	1 cm x 0.75 cm size silver/gray "pellets"		11.248 g
Krazy Kids #C	1 cm x 0.75 cm size silver/gray "pellets"		11.293 g
KP/Al standard	fine gray powder		
KC/Al standard	fine gray powder		
KP/KC/Al standard	fine gray powder		
RDX standard	fine white powder		
PETN standard	fine white powder		

The standards used in this work were of two distinct types. PETN (pentaerythritol tetranitrate) and RDX (cyclotrimethylenetrinitramine) are military grade explosives used to calibrate the instruments used to establish sensitivity to mechanical insult. It is a standard practice to compare the behavior of unfamiliar materials with those of PETN; PETN is considered to be either a relatively insensitive primary explosive, or one of the most sensitive secondary explosives, and is thusly used to give a boundary between those two classes. PETN may be detonated by striking with a hammer on a hard steel surface, and is generally considered the least sensitive explosive with which this may be done. RDX is only slightly less sensitive to mechanical insult. By comparing the sensitivity of an explosive against the behavior of PETN, therefore, it may be determined whether or not the material can be classified as a primary or secondary explosive. This determination will impact the ability to safely handle the material, and give considerations on how this would be done.

The second type of standards serves several purposes. The three homemade flash powders are stoichiometric mixtures of finely divided aluminum powder (Al) and potassium chlorate (Al + $KClO_3$), potassium perchlorate (Al + $KClO_4$) or a mix of the two (Al + $KClO_3$ and $KClO_4$). These materials are used to assure good detection of these important chemicals, which may be found in all the flash powder types of samples, to understand endothermic behavior in the thermal testing (as the oxidizers melt), to demonstrate the susceptibility to mechanical insult of sulfur-free flash powders, and to provide at least one sample that would analyze positively for chlorate.

Other calibration verification standards were used in the chemical analysis and thermal testing. If those samples fell within appropriate limits, they are not discussed in this report.

The primary objective of this work is to establish the relative sensitivity of each sub-sample as related to the chemistry of the material. Both the sensitivity to mechanical insult and the chemical composition were carefully evaluated, in comparison with the behavior of the standard materials and common recipes for amateur pyrotechnics production. Taken together, the measurements indicate that the samples provided are within the range of ordinary published formulations.

4.0 Experimental Methods and Procedures

4.1 Handling Precautions

Fireworks components are known to be extremely sensitive to mechanical insult (i.e. impact, friction and electrostatic discharge). Flash powder, a mixture of finely divided metal powder and oxidizer, in particular is recognized by authors in the amateur pyrotechnics community, as being particularly dangerous: ***"The first rule of caution is to note that compositions are extremely hazardous when subjected to heat, friction, sparks, static electricity or a sharp blow. Mixing or manufacturing flash compositions is possibly more dangerous than attempting to manufacture black powder, improvised plastic or other nitrate type explosives."***[4] Because flash powders are a component found in nearly every pyrotechnic device, all the samples were treated as a significant hazard. In spite of the limited amounts of material delivered as samples, an accident with any one of them could have resulted in disfiguring injuries for those involved. Therefore, we used all the normal safety precautions exercised in an explosives laboratory.

The technicians performing the testing wore fireproof lab coats, laboratory glasses, nitrile gloves and grounding heel straps during the performance of this work. Additionally, when doing the sample processing, they were also wearing wrist grounding straps. When running the actual mechanical insult test series, they used hearing protection, in this case earplugs. No persons uninvolved with the testing were permitted in the lab when the samples were not locked in storage. Normal safety precautions of banning spark-producing devices and cell phones from the lab were observed.

The samples were stored in an ATF-approved explosives magazine. Chains of custody (included in the delivered materials) were utilized every time the samples were removed from the magazine, such that every usage of the material was documented. NCOI forms were signed by all technicians who took part in the program.

A standard operating procedure including safety protocol and PPE requirements was written from the military standards and the samples were processed and tested for mechanical insult sensitivity at the ARA office in Panama City, FL.

4.2 Sample Preparation

This section describes the preparation of all samples for each specific test.

4.2.1 Sample Preparation for Mechanical Insult Testing

The samples with larger particle size distributions needed to be safely processed into a powder form prior to testing. The military standard specifies that the tests be performed on a particular sample quantity not possible on the large chunks present in some of the sub-samples. For the specimens not delivered as a fine powder, a processing technique was developed.

To eliminate possible friction hazard, the process was performed on a plastic sheet over a paper towel, rather than on a metallic surface. This treatment provided an extra cushion that kept the applied impact to a minimum. Large sample particles were first cut into smaller pieces with a razor blade, and the resulting chunks crushed into a powder form with a non-sparking metal spatula. This process is shown in Figure 2 and the results in Figure 3. To keep the direct forces to a minimum, a small rolling action over the chunks generated a powder of more appropriate particle sizes. On every sample, this technique worked very well in producing a coarse powder (Figure 4). These powders, along with those samples that had arrived as powdered material, were submitted to the testing.

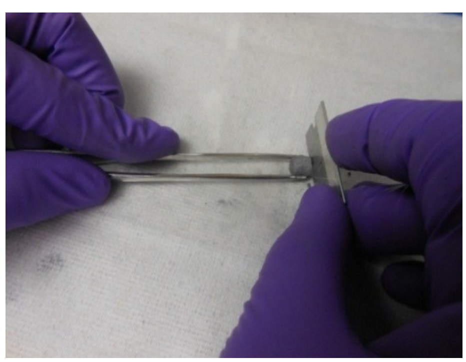


Figure 2. Photo of initial cutting procedure.

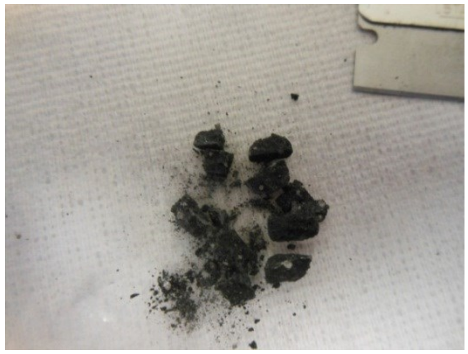


Figure 3. Initial processing of the larger samples; chopping with a razor blade.

Figure 4. Completely processed powder.

4.2.2 Sample Preparation for Chemical and Thermal Testing

In preparations for SEM and EDAX, a small amount of the powder was removed from the container via spatula. Carbon tape was then lightly pressed against the powder, tapping off any loose power, leaving a thin monolayer of powder stuck to the tape. The carbon tape with the sample on it was then placed directly on the sample platform in the SEM. The carbon tape is composed largely of carbon and oxygen, and its use negates any information about these elements in the EDAX elemental composition data. The other reported elements come from calibrated signal channels.

In the analysis of a single-phase, pure element, sample at 15 kV the smallest possible interaction volume is about 1 μm in diameter. Elements with atomic number higher than that of Na are well analyzed with this technique, and have detection limits in the range of $1/10^4$ to $1/10^5$. Actual interaction regions are slightly more diffuse with the real samples, which are heterogeneous in both composition and morphology.

Regions where the electron beam is incident on the sample range from the very tightest focus (used to identify the composition of individual particles) to full-image (used to establish overall sample composition). Regions marked in some SEM images in the results section indicate the location of the interaction region, but not necessarily the size of the spot probed with EDAX. EDAX results are normally viewed as semi-quantitative, and are used in this work to establish presence or absence of certain materials, rather than the absolute concentration of them.

Sample preparation for the ICP analysis consisted of 1 mg of sample being put into 10 ml of deionized water (DI). 1 ml of this slurry was then added to 10 ml of HNO_3. Note that no sample digestion was performed, as this data was viewed largely as a simple confirmation of EDAX results. In these results, scandium (Sc) was used as an internal standard, and several of the channels were not calibrated. This latter fact explains the presence of positive readings in the uranium channels, rather than the actual presence of uranium.

Analysis of anions was performed by chromatographic techniques: Samples for the anion analyses were put into deionized water (DI), 0.25 g into 25 ml. Analyses were performed on filtered solution. No preservatives were used.

IR spectroscopy was also used to analyze anions. This analysis was done with wetted samples largely to eliminate possible safety problems of squeezing the sample material between the sample holder and the pressure clamp. The sample holder allows the attenuated total reflectance to be measured through the sample. ATR-FTIR samples were generated by putting 1 mg of each sample into 10 ml of DI. This solution was thoroughly shaken and allowed to settle. 9 ml of liquid was removed, leaving behind a dense slurry of sample and DI. A disposable pipette was used to add 1 drop of the slurry to the diamond surface in the center of the metal sample holder on the FTIR and the IR tip was lowered onto the holder, pinning a thin layer of slurry between the tip and the holder. Blank backgrounds were collected prior to sample analyses.

Thermal stability testing: Sample sizes of approximately 1 mg were directly put into sample pans and hermetically sealed before analysis in the differential scanning calorimeter (DSC).

Figure 5. MBOM Impact Testing Machine

4.3 Brief Test Descriptions of All Tests

4.3.1 Mechanical Insult Test – Impact.

To establish sample sensitivities to initiation by impact, the Modified Bureau of Mines (MBOM) Impact test machine was used, shown in Figure 5. MBOM Impact test machine creates high impact forces on energetic materials. The machine's impacting mass (2.5 kg) is dropped from programmable heights (up to 100 cm) before striking a sample situated on a steel anvil. The combined effects of impact and confinement ignite the material at heights that provide energy above the reactive threshold. Reaction of the material is determined by observation and/or examination of the sample residue.

In order to determine the relative impact sensitivity, the "Bruceton" or "Stair-step" method of initiation threshold identification is performed. A 25 ± 5 mg sample of material is placed on 1 inch square 180 grit sandpaper in a small pile under the striker. The drop weight of 2.5 kg is set at the determined height. While observing the sample area, the drop weight is released via electromagnet. After recording the reaction as a "go" or "no go", the drop weight is removed from the striker and the anvil and striker faces are cleaned. A "go" is determined by the operators observing smoke, flash, flame, sparks, or a loud report to differentiate it from regular machine noise. As per the "Bruceton" testing method, when a "go" is recorded, the operator sets the next test height to the next lower log interval. If a "no go" is recorded, the operator sets the next test height to the next higher log interval. The operator repeats this process 25 times. These numbers yield a $H_{50\%}$, or height where the sample will react 50% of the time. Calibration standards of RDX and PETN were run in this machine, and results well within the accepted limits of the military method were obtained. Testing was conducted in accordance with MIL-STD 1751A Method 1021.[5]

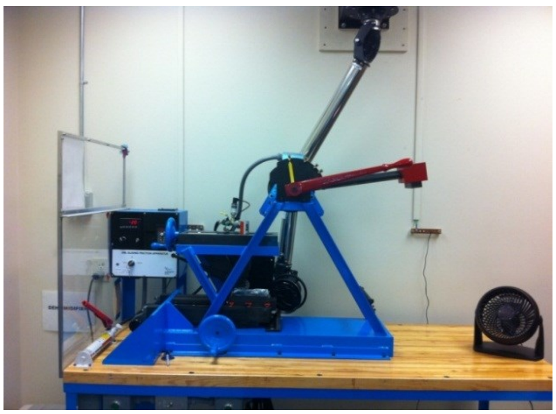


Figure 6. ABL Friction Testing Machine

4.3.2 Mechanical insult test – Friction

ARA used an Allegheny Ballistics Laboratory (ABL) Friction Test Apparatus for conducting these tests, shown in Figure 6. The apparatus delivers a sliding friction input into a small sample (nominally 10 mg) of test material. The primary parts of the test apparatus are a friction wheel that applies a load to the sample and a friction plate upon which the test sample is placed. An explosive sample is positioned on the friction plate; the friction wheel is lowered onto the sample at a pre-determined load, such that the sample is pinched between the plate and the wheel. The pendulum weight is raised to the 8 feet per second height and locked in place by an electromagnetic brake. When ready to test, the brake is released, and the pendulum weight impacts the friction plate causing it to slide rearwards.

Figure 7. ABL Friction Machine, showing a positive result

Initiation of the sample is determined by production of an audible pop, flame or smoke, as shown in Figure 7. This test simulates potential initiation of explosive that may be caught in mechanical parts, which could apply a pinch or sliding load on the explosive. Solids, liquids, or powders can be tested with this apparatus. Testing was conducted in accordance with MIL-STD 1751A Method 1021.[5]

4.3.3 Electrostatic Discharge test

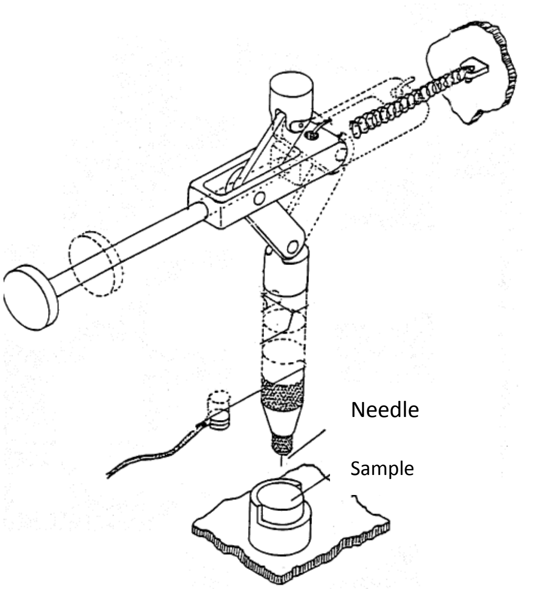


Figure 8. Detail of electrode assembly of ESD testing machine.

Total energy deposited in a human ESD event is reported to be tens of millijoules (mJ).[6] Giving a safety factor of approximately 10x, any material initiated with discharges under 0.25 joules is normally classified as hazardous. Most explosives and pyrotechnics are hazardous to an electrostatically generated spark. A quantitative measure of sensitivity to spark is determined by the electrostatic discharge (ESD) test. The ABL ESD machine operates by generating an electric charge in a bank of capacitors across an electron gap at 5,000 VDC (Figure 8. Detail of electrode assembly of ESD testing machine.). The electric charge is discharged through a sample of the test material held on a grounded Teflon plate. The discharge point is a needle of specific design that is lowered toward the sample. As the distance between needle and the grounded plate narrows, the electricity arcs from the needle to the grounded plate. The electric arc passes through the test sample resulting in a reaction or non-reaction of the material. The whole apparatus is shown in Figure 9.

The goal of the ESD test is to find the threshold of initiation level (TIL). This is the highest level of electrical energy (joules) at which 20 consecutive "no gos" are recorded. The operator places approximately 10 mgs of the test material on the platform. The appropriate capacitor is selected by the turn of two knobs and is charged to 5000 Vdc. The operator fires the machine and observes. If results are negative, i.e., no reaction, the test is continued until 20 consecutive "no-gos" are reported. If the test sample has a positive result, i.e., flash, spark, burn, odor, or noise other than instrument noise, then testing should be performed at the next lower level until 20 consecutive "no-gos" are reported. The final number is reported as number of "no gos" out of 20 at the tested power level; for example "0/20 "No Gos" @ 0.19 Joules."

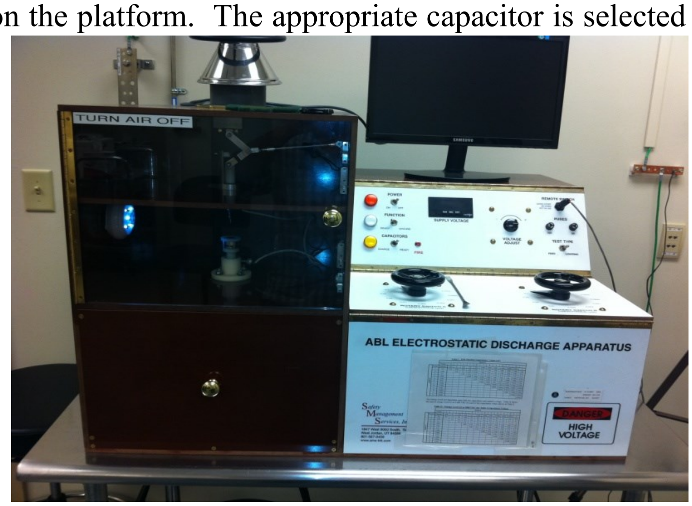


Figure 9. ABL Electrostatic Discharge Testing Machine.

4.3.4 Scanning Electron Microscope – Energy Dispersive X-ray (SEM-EDAX) Analysis

SEM is a type of high-magnification imaging in which the sample is scanned with a focused beam of electrons. These electrons typically interact with the sample material on an atomic level, yielding information about the material's morphology (in the case of the fireworks samples, particle size and heterogeneity). Detection is performed through observation of an image of secondary electrons emitted from the sample after having been excited by the input beam. These images are not natively colored, because no light of visible wavelength is involved. The images are typically shown in black and white. When excited by the electron beam, X-rays characteristic of the atomic composition of the sample are also emitted, which forms the basis of the X-ray elemental analysis. The instrument was run under a relatively high-pressure and humidity environment, enabling imaging of materials sensitive to electrostatic discharge to be performed.

4.3.5 Inductively Coupled Plasma Atomic Emissions Spectroscopic (ICP-AES) Analysis

ICP-AES, also called ICP-optical emission spectrometry (ICP-OES) is a type of emission spectroscopy that uses a high-temperature plasma to excite atoms in a sample to highly excited states or to create ions. These excited or ionized atoms emit light at frequencies characteristic of their elemental composition. Detection of this light is used to determine the trace elements present in a sample. For this analysis, samples are typically dissolved or digested into an acidic aqueous matrix that is fed into the plasma torch through a nebulizer that sprays the matrix into the torch as an aerosol. Results are generated by comparing the amount of light produced at each of a number of wavelengths to those generated from a known amount of that same element from a standard.

4.3.6 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

In FTIR analysis, the absorbence of light in the IR region by the sample is measured. This type of instrument uses a broadband infrared source coupled with wavelength deconvolution with a Michelson interferometer to determine which molecular features are present from the sample. In the fireworks, FTIR is principally used for identification of anions in powdered salts, like the nitrate in potassium nitrate (NO_3^-). The output spectra often has units of % transmission vs wavenumber. In this case, because of the sensitivity of the samples toward impact and friction, they were presented to this instrument dissolved in water.

4.3.6 Differential Scanning Calorimetry (DSC) Analysis

Differential scanning calorimetry is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The basic principle underlying this technique is that when the sample undergoes a physical transformation such as phase transitions, more or less heat will need to flow to it than the reference to maintain both at the same temperature. Whether less or more heat must flow to the sample depends on whether the process is exothermic or endothermic. Although the endothermic events result in remarkable data in this work, chiefly we are interested in exothermic behavior indicative of decomposition.

5.0 Data, Observations and Results

In this section, the results of the chemical composition testing will be presented sample by sample, and then compared with each sample's sensitivity to initiation by mechanical insult. A small percentage of the data, mostly SEM images, are presented here to guide the reader.

The section is organized into two tables of overall results. Table 2 is organized by sample name. Table 3 presents the same information broken down by sample type. Following the tables, each individual material is addressed. The results section for each material is structured into a description of the sample, both visual and SEM. The EDAX results are related to the SEM image, and here the overall composition is given, rather than the composition of individual particles, unless they are exceptional. Many other SEM-EDAX results are available on each material in the Appendix. Because of the heterogeneity of the powders, the EDAX should be considered a semi-quantitative measurement, a sort of overall average of the material seen in the SEM image. As previously mentioned, although oxygen and carbon values are given in the EDAX results, these numbers are probably not useful, because of the contribution of these signals from the tape used to present the sample to the testing.

ICP data given in this section is largely a "presence or absence" measurement, a correlative study looking for agreement with the EDAX work. The samples were not digested prior to the testing, and therefore materials not soluble in water will appear only weakly, or not at all. However, in every case, good agreement was established between the elemental composition data from the EDAX and the ICP.

FTIR and chromatographic analysis used to determine anions were also a correlative pair. In this case, the primary measurement was IC (for chlorate and nitrate) and LCMS (for perchlorate). These should also be considered semi-quantitative results, because of the small amount of material used to create the slurry for testing (FTIR) and the filtered solution used in the chromatographic analyses. It is unknown if sample heterogeneity can be adequately represented by samples as small as those we received

The chief result from thermal testing is the decomposition temperature of small quantities of sample material. The testing takes the sample from room temperature to 500 °C at a rate of 20 °C per minute. Interesting data is also obtained from lower temperature endotherms where chemical components of the sample undergo crystal rearrangement or melt. These exact temperatures vary with sample particle size, and also the presence of the other components in the sample matrix. DSC thermograms are shown on only a few of the individual sample descriptions, in order to save space. All the others are available in the Appendix.

The mechanical insult testing yields a value for each type of possible initiation; impact, friction and electrostatic discharge. These values are used to compare the behavior of the sample with those of the standards, in order to classify the samples as more (or less) dangerous to handle than military explosives that are often considered the least reactive primary explosives (PETN and RDX). A non-detect (ND) is reported if the sample is not sensitive to that particular stimulus.

Results ordered by sample name are given in Table 2. Results that have been presented by type of material are shown in Table 3.

Table 2. Compiled Results of Testing by Sample Name

Name of sample	Physical Description	Impact ($H_{50\%}$)	Friction ($F_{50\%}$)	ESD (joules)	Major cations	Major anions	Sulfur %/wt	Thermal decomp onset
Units		cm	psi	0/20 at				°C
O-Triple C #A	fine gray sparkly powder	62	9	0.063	Mg, Al, K, Ti	ClO_4^-	2.5	>500
O-Triple C #B	small black pebbles	ND	ND	0.25	K	NO_3^-	5-32	365
O-Triple C #C	"BB" size round silver/gray balls	12	13	0.063	Mg, Al, K, Ti	ClO_4^-, NO_3^-	4-30	355
Sky Festival #A	large gray pellets w/ black & brown crumbs	22	9	0.063	Mg, Al, K, Cu	ClO_4^-	14	361
Sky Festival #B	large gray pellets w/ black & brown crumbs	14	15	0.025	Mg, Al, K, Sr, Ca	ClO_4^-	1.2	>500
Sky Festival #C	fine gray sparkly powder	ND	9	0.025	Mg, Al, K	ClO_4^-	ND	>500
Sky Festival #D	fine gray sparkly powder	ND	9	0.025	Mg, Al, K, P Ca, Si, Fe	ClO_4^-	ND	>500
Sky Festival #E	black particles, about 0 .5 mm across with copper colored dust	ND	ND	0.63	K	NO_3^-	14	Not tested
Sky Festival #F	copper colored powder with black particles	Not tested	Not tested	Not tested	K, Si, Al and Fe	NO_3^-	ND	Not tested
Sky Festival #G	grayish coarse powder	20	9	0.25	Al, Mg, Sr, K	ClO_4^-	1.7	Not tested
Halawa #A	small black pebbles	ND	ND	0.063	K	NO_3^-	8	363
Halawa #B	fine gray powder, with larger chunks	50	9	0.013	Mg, Al, K, Ti, Si	ClO_4^-	2.4	>500

Name of sample	Physical Description	Impact ($H_{50\%}$)	Friction ($F_{50\%}$)	ESD (joules)	Major cations	Major anions	Sulfur %/wt	Thermal decomp onset
Units		cm	psi	0/20 at				°C
Halawa #C	fine gray powder	72	9	0.063	Mg, Al, K, Ti	ClO_4^-	4-13	>500
Krazy Kids #A	small black pebbles	ND	ND	0.25	K, Al	NO_3^-	10	363
Krazy Kids #B	1 cm x 0.75 cm size silver/gray "pellets"	28	265	0.063	K, Al, Ba	ClO_4^-, NO_3^-	12	354
Krazy Kids #C	1 cm x 0.75 cm size silver/gray "pellets"	23	134	0.13	Mg, Al, K, Sr, Ca	ClO_4^-, NO_3^-	7	353
KP/Al	fine gray powder	60	77	0.013	Al, K	ClO_4^-	ND	Not tested
KC/Al	fine gray powder	71	71	0.013	Al, K	ClO_3^-	ND	Not tested
KP/KC/Al	fine gray powder	55	77	0.013	Al, K	ClO_4^-, ClO_3^-	ND	>500
RDX	fine white powder	19	11	0.063	Not tested	Not tested	Not tested	Not tested
PETN	fine white powder	12	13	0.063	Not tested	Not tested	Not tested	Not tested

Table 3. Results segregated by sample type

Name of sample	Physical Description	Impact ($H_{50\%}$)	Friction ($F_{50\%}$)	ESD (joules)	Major cations	Major anions	Sulfur	Thermal decomp onset
Units		cm	psi	0/20 at				°C
	Flash powders without sulfur do not thermally decompose < 500 °C							
O-Triple C #A	fine gray sparkly powder	62	9	0.063	Mg, Al, K, Ti	ClO_4^-	2.5	>500
Sky Festival #C	fine gray sparkly powder	ND	9	0.025	Mg, Al, K	ClO_4^-	ND	>500
Sky Festival #D	fine gray sparkly powder	ND	9	0.025	Mg, Al, K, Ca, Si, Fe, P	ClO_4^-	ND	>500
Halawa #B	fine gray powder, with larger chunks	50	9	0.013	Mg, Al, K, Ti, Si	ClO_4^-	2.4	>500
Halawa #C	fine gray powder	72	9	0.063	Mg, Al, K, Ti	ClO_4^-	4-13	>500
KP/Al	fine gray powder, standard	60	77	0.013	Al, K	ClO_4^-	ND	Not tested
KC/Al	fine gray powder, standard	71	71	0.013	Al, K	ClO_3^-	ND	Not tested
KP/KC/Al	fine gray powder, standard	55	77	0.013	Al, K	ClO_4^-, ClO_3^-	ND	>500
	Lift charges (black powders) are not sensitive to impact or friction.							
Halawa #A	small black pebbles	ND	ND	0.063	K	NO_3^-	8	363

Name of sample	Physical Description	Impact ($H_{50\%}$)	Friction ($F_{50\%}$)	ESD (joules)	Major cations	Major anions	Sulfur	Thermal decomp onset
Units		cm	psi	0/20 at				°C
O-Triple C #B	small black pebbles	ND	ND	0.25	K	NO_3^-	5-32	365
Krazy Kids #A	small black pebbles	ND	ND	0.25	K, Al	NO_3^-	10	363
Sky Festival #E	black particles, about 0 .5 mm across with copper colored dust	ND	ND	0.63	K	NO_3^-	14	Not tested
	"Stars" and "comets" - sulfur usually sensitizes flash powder to both mechanical insult and thermal decomposition.							
O-Triple C #C	"BB" size round silver/gray balls	12	13	0.063	Mg, Al, K, Ti	ClO_4^-, NO_3^-	4-30	355
Sky Festival #A	large gray pellets w/ black & brown crumbs	22	9	0.063	Mg, Al, K, Cu	ClO_4^-	14	361
Sky Festival #B	large gray pellets w/ black & brown crumbs	14	15	0.025	Mg, Al, K, Sr, Ca	ClO_4^-	1.2	>500
Sky Festival #G	grayish coarse powder	20	9	0.25	Al, Mg, K, Sr	ClO_4^-	1.7	Not tested
Krazy Kids #B	1 cm x 0.75 cm size silver/gray "pellets"	28	265	0.063	K, Al, Ba	ClO_4^-, NO_3^-	12	354
Krazy Kids #C	1 cm x 0.75 cm size silver/gray "pellets"	23	134	0.13	Mg, Al, K, Sr, Ca	ClO_4^-, NO_3^-	7	353
	The following sample appears to be pyrotechnic clay, used to separate sections and guide gas emission.							
Sky Festival #F	copper colored powder with black particles	Not tested	Not tested	Not tested	K, Si, Al and Fe	NO_3^-	ND	Not tested

Name of sample	Physical Description	Impact ($H_{50\%}$)	Friction ($F_{50\%}$)	ESD (joules)	Major cations	Major anions	Sulfur	Thermal decomp onset
Units		cm	psi	0/20 at				°C
	These samples are calibration samples for the mechanical insult testing machines.							
RDX	fine white powder	19	11	0.063	Not tested	Not tested	Not tested	Not tested
PETN	fine white powder	12	13	0.063	Not tested	Not tested	Not tested	Not tested

5.1 O-Triple-C Results

5.1.1 Sample O-Triple-C, Sub-sample A

This sample is a silvery gray powder that contains white flakes (0.2 - 0.5 mm in length). 5.157 g of this material was delivered. These white flakes are easily seen in an enlarged version of the optical photograph, Figure 10, and even more so in the 40x magnified SEM image (Figure 11). These white flakes are present in a matrix of darker pellets. The appearance is similar to that of the flash powder standards.

Figure 10. Enlarged photograph of O-Triple-C, A.

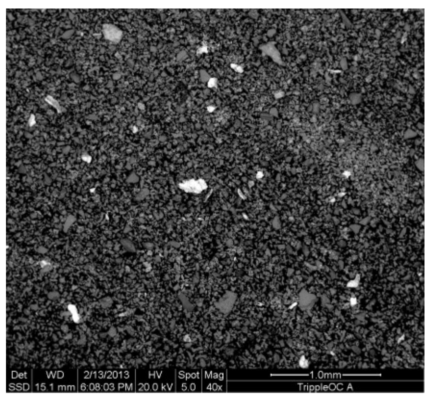


Figure 11. 40x SEM image of O-Triple-C, A.

The SEM-EDAX analysis of O-Triple-C A is shown below (Figure 12). The top composition analysis was performed on the wide particle that takes up most of the micrograph. This particle is composed of titanium, with hints of other metal particles. Titanium is used in fireworks to make bright whitish sparks, and magnesium and aluminum are also common components of flash powders. The smaller particles that appear darker in the micrograph are heavily laden with chlorine, making up the other chief component of common flash powders, the oxidizer component.

The chlorine in the sample was found as perchlorate, observed in both FTIR and LC/MS data. No chlorate or nitrate anions were observed. The ICP data confirms the presence of K (likely the cation associated with the perchlorate), Mg and Al, but does not find Ti. This is due to the insolubility of the metal particles in the light acid treatment used to dissolve the sample in water for introduction to the ICP. Chemical composition shows this sample appears to be a flash powder, with some additional metal dust that may serve to make streamers in the final pyrotechnic product. This sample is quite sensitive to various forms of mechanical insult, as is discussed in the section on mechanical insult below, but does not decompose when heated, as shown by DSC results.

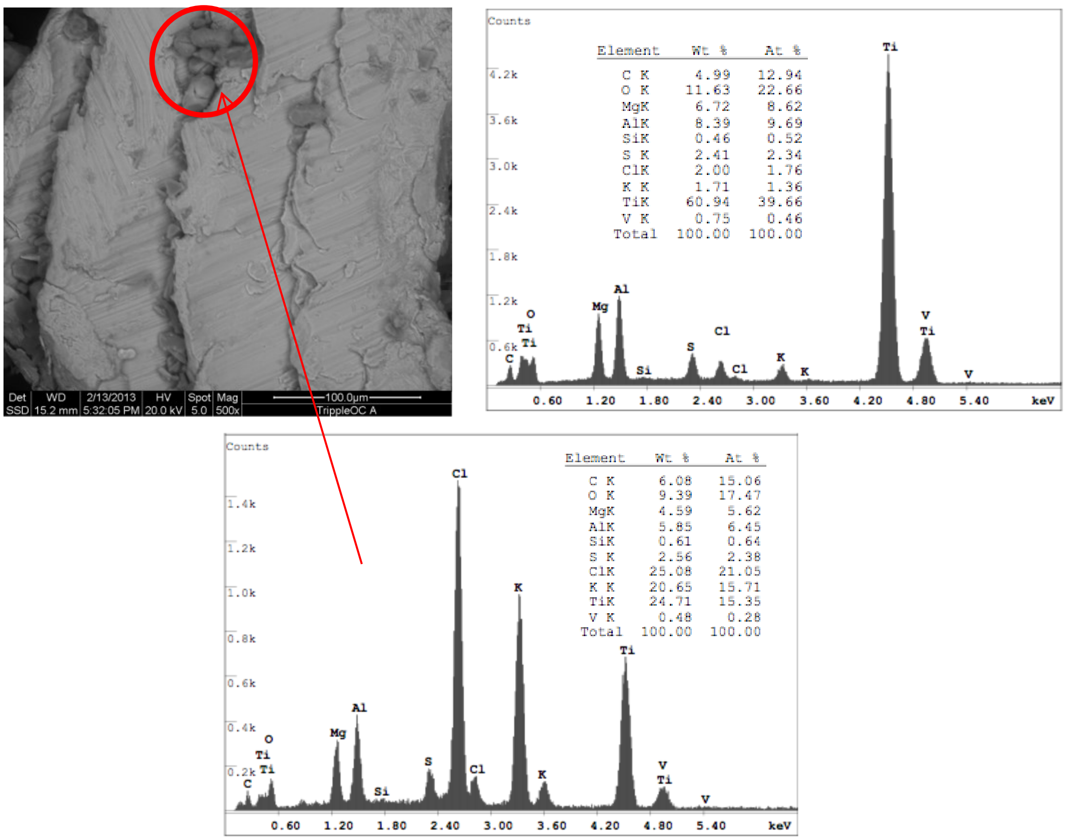


Figure 12. SEM and EDAX data of O-Triple-C, A.

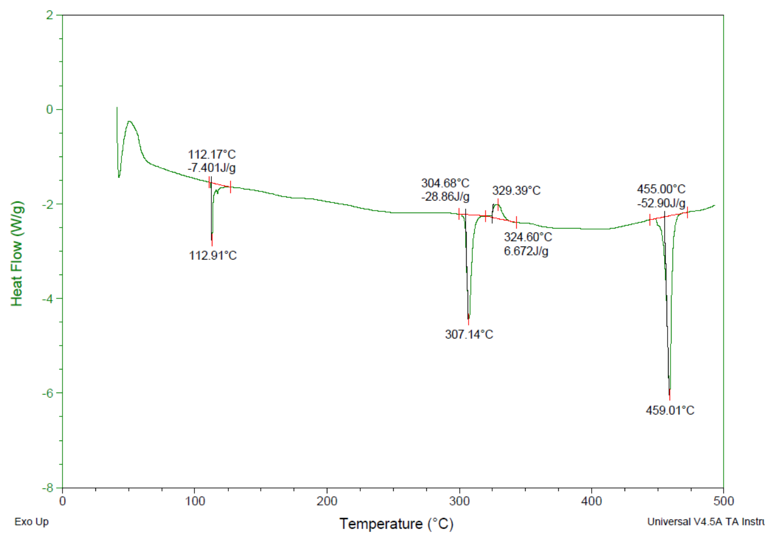


Figure 13. DSC results for O-Triple-C, A, showing no thermal decomposition below 500 degrees C.

Data Summary of O-Triple-C A:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 62 cm
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.063 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K and flakes of Ti
- Predominant metals (ICP-AES) – Mg, Al, K
- Anion(s) – perchlorate
- Other species – S (2.5%/wt)

Thermal Sensitivity Data

- DSC exotherm – NA
- Other DSC features – endotherms at 112 and 305 °C indicate sulfur melting point or loss of water and $KClO_4$ crystal phase transition, respectively. The endotherm at 455 °C may be related to sulfur volatilization (reported to boil at 444.6 °C)

This material is a flash powder, having a normal composition compared to recipes on amateur fireworks websites given the data obtained during the testing. As such, it is very sensitive to initiation by ESD and frictional forces.

5.1.2 Sample O-Triple-C, Sub-sample B

This sample is composed of black pebbled material, as shown in an enlarged photograph in Figure 14. 8.294 g of this material was delivered. It has the overall appearance of black powder and there were pieces of fuse material delivered with the sample. The fuse material was not analyzed.

Figure 14. Enlarged photo of O-Triple-C, B.

SEM shows it to be composed of large particles, and EDAX (Figure 15) taken across the entire field of view demonstrates that it is free of any chlorine compound, a result that is mirrored in both the FTIR and the anion (IC) analytical data. Instead, this sample contains nitrate, which is most likely the counter-ion to the potassium, and sulfur. Black powder has the general recipe of potassium nitrate (KNO_3), sulfur and charcoal, which mirrors the composition found in this sample. ICP analysis verifies the presence of the potassium and the absence of any meaningful amount of any other metals.

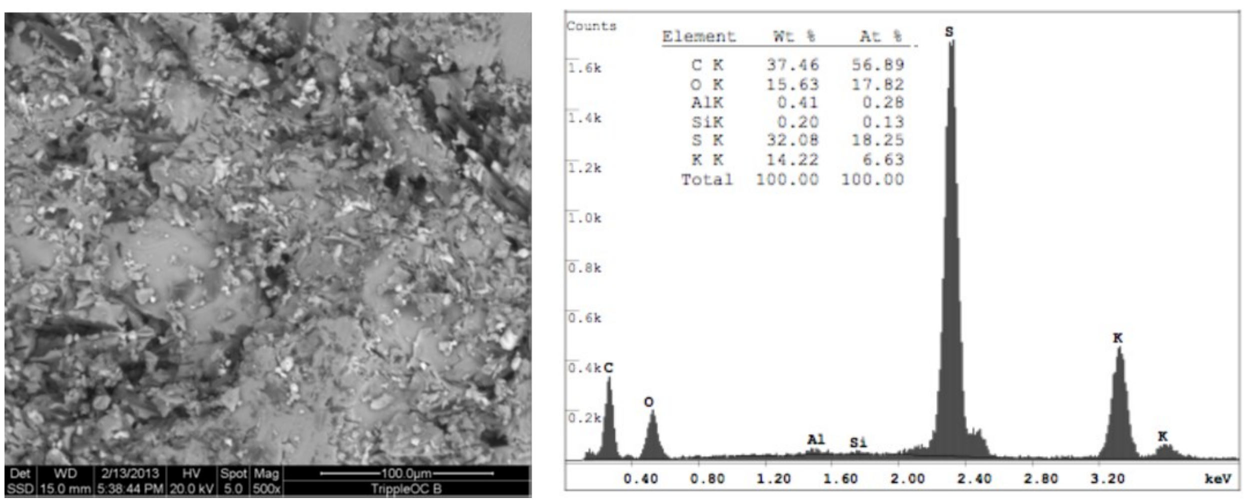


Figure 15. SEM and EDAX data, O-Triple-C B.

EDAX results collected from white regions in the SEM image result in a heavier potassium signal but not chlorine, which likely indicates that the white regions in the image are KNO_3 crystals. Additionally, EDAX results from the grayish portions of the SEM image (as distinct from the smaller black particles) are even heavier on the potassium signal. The sulfur peak is smaller, perhaps indicating a lack of sulfur in the light smoother grayish places on the image.

This sample is quite heterogeneous, which is related to the wide range of sulfur measurements received in EDAX results. There was no "large area" EDAX taken for this particular sample, and therefore the range of the sulfur results is reported, rather than one that is representative of the sample as a whole.

DSC results indicate that this sample begins to decompose when heated past 365 °C.

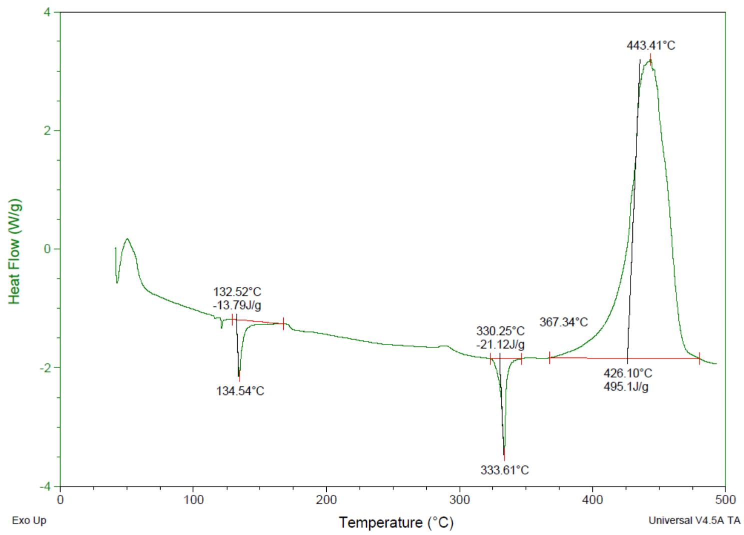


Figure 16. DSC data from O-Triple-C, B. Sample decomposition onset at 365 degrees C.

Data Summary of O-Triple-C B:

Mechanical Insult Data

- Impact ($H_{50\%}$) – No initiation observed
- Friction ($F_{50\%}$) – No initiation observed
- ESD (Joules) – 0.25 J

Primary Chemical Results

- Predominant metals (EDAX) – K
- Predominant metals (ICP-AES) – K
- Anion(s) – nitrate
- Other species – sulfur (5-32%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 365 and peaking at 437 °C is indicative of decomposition
- Other DSC features – endotherm at 132 °C is likely a KNO_3 (α to β) crystalline phase change. The endotherm at 330 °C is KNO_3 melting.

This sample appears from the presented data to be a lift charge; a variety of black powder. As such, it is less sensitive to initiation by mechanical forces than the flash powder samples that were analyzed.

5.1.3 O-Triple-C, Sub-sample C

This sample is composed of grayish powder and larger gray chunks. 10.241 g of this material was delivered. This sample is composed of a silvery gray powder and round gray balls a few mm in diameter. Figure 17 is an enlarged photograph of the sample material in a Velostat container. The larger particles were processed into powder with a razor blade at the time of the mechanical insult testing, and this prepared sample was also used to acquire SEM and EDAX data (Figure 18).

Figure 17. Enlarged photo of O-Triple-C, C.

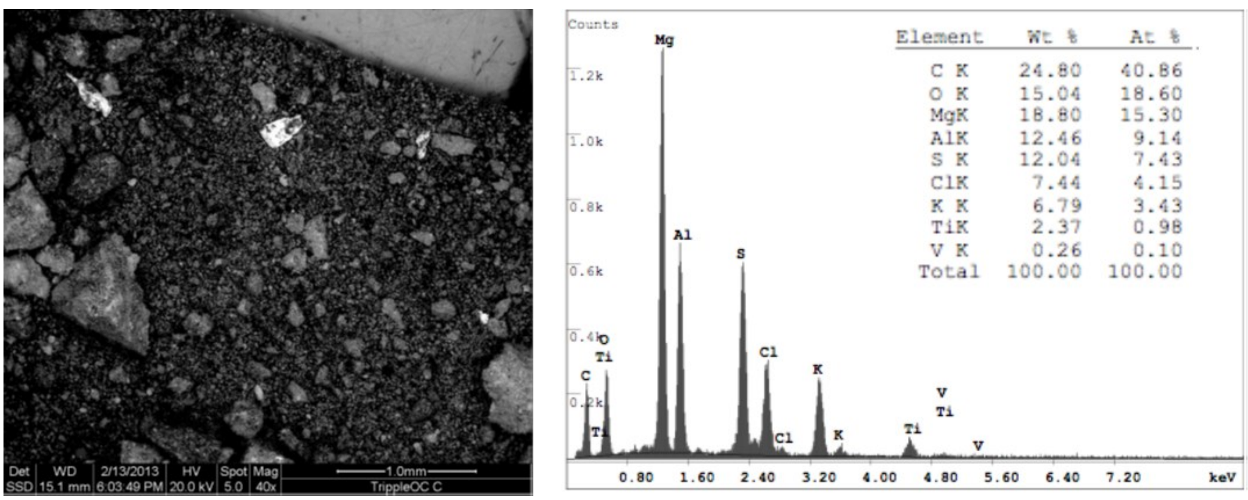


Figure 18. SEM and EDAX data for O-Triple-C, C.

EDAX on the entire region of the SEM image is dominated by metal powders (Al and Mg) and sulfur. Potassium is also present. The composition of metals is confirmed in the ICP data. Chlorine is also extant, as perchlorate, indicated in the anion analysis (LC/MS) and FTIR spectrum. Nitrate is present in a smaller quantity (seen in LC/MS data). EDAX analysis of the large white spade-shaped particle in the Figure 18 image yields a very high concentration of titanium.

This sample is quite heterogeneous, which is related to the wide range of sulfur measurements received in EDAX results. There was no “large area” EDAX taken for this particular sample, and therefore the range of the sulfur results is reported, rather than one that is representative of the sample as a whole.

DSC results indicate that this sample begins to decompose when heated past 355 °C.

Data Summary of O-Triple-C C:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 12 cm
- Friction ($F_{50\%}$) – 13 psi
- ESD (Joules) – 0.063 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K and flakes of Ti
- Predominant metals (ICP-AES) – Mg, Al, K
- Anion(s) – perchlorate, smaller quantity of nitrate
- Other species – sulfur (4-30%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 355 °C and peaking 403 °C is indicative of decomposition
- Other DSC features – endotherm at 305 °C indicates a $KClO_4$ crystal phase transition.

This material appears to be pyrotechnic “star” or “comet” material, which is flash powder mixed with sulfur and various materials to cause the chunks to adhere together. Sulfur is a known sensitizer of flash powder, causing even higher degrees of sensitivity to initiation by mechanical insult, as well as to thermal decomposition. This sensitization is clearly observable in the data from this material. Even so, sulfur is a common component of pyrotechnic material and its presence is no way indicative of special compounding.

5.2 Sky Festival Samples

5.2.1. Sky Festival Sub-sample A

2.473 g of this material was delivered. It is composed of large gray pellets intermixed with smaller black and brown particulate. This material was processed into smaller particles for testing. These larger chunks are probably “stars” or “comets.” An enlarged photo of this material is shown in Figure 19.

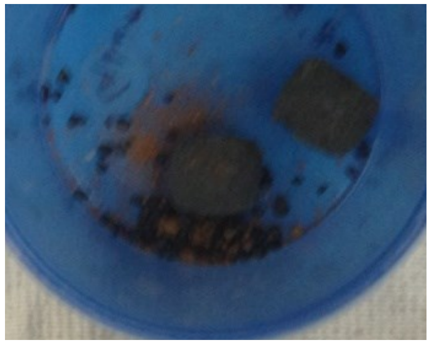
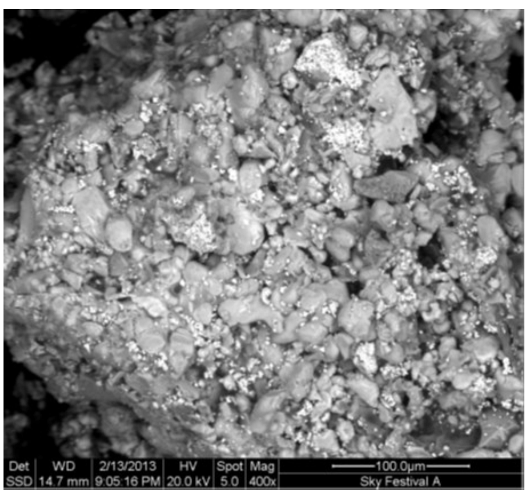


Figure 19. Enlarged photo of Sky Festival A sample.

This sample was found to be as sensitive to initiation by mechanical insult and ESD as the other flash powder-type samples. X-ray analysis (Figure 20) yields a composition very similar to the O-Triple-C C sample, which was delivered with similar physical appearance, having peaks associated with sulfur, chlorine, potassium, magnesium and aluminum. The presence of these components is confirmed in the ICP data and in LC/MS data, which indicates a high concentration of perchlorate. Both EDAX and ICP data show copper and chromium, likely coloring agents for the pyrotechnic materials.

DSC results indicate that this sample begins to decompose when heated past 361 °C.



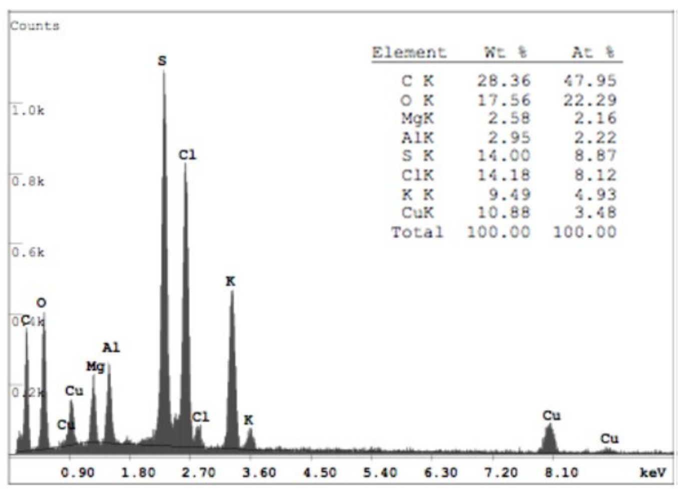


Figure 20. SEM and EDAX data of Sky Festival A.

Data Summary of Sky Festival A:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 22 cm
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.063 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K with smaller amounts of Cu

- Predominant metals (ICP-AES) – Mg, Al, K, small amounts of Cu and Cr
- Anion(s) – perchlorate
- Other species – sulfur (14%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 361 and peaking at 411 °C
- Other DSC features – endotherm at 305 °C indicates a $KClO_4$ crystal phase transition.

5.2.2. Sky Festival Sub-sample B

Sample B is also composed of large gray pellets intermixed with small black and brown particles. 2.482 g of this material was delivered. This material was processed into smaller particles for testing. These larger chunks are likely to serve as "stars" or "comets" when built into a pyrotechnic device. An enlarged photo of the material is shown in Figure 21.

Figure 21. Enlarged photo of Sky Festival B.

This sample was found to be as sensitive to initiation by mechanical insult as the other sulfur-laden flash powder-type samples. X-ray analysis (Figure 22) yields a composition very similar to the Sky Festival A sample, having peaks associated with sulfur, chlorine, potassium, magnesium and aluminum. The presence of these components is confirmed in the ICP data and in IC/MS data, which indicates a high concentration of perchlorate. Both EDAX and ICP data show strontium, likely a coloring agent for the materials. The material also contains calcium, found in both EDAX and ICP data.

DSC results indicate that this sample does not decompose at temperatures less than 500 °C.

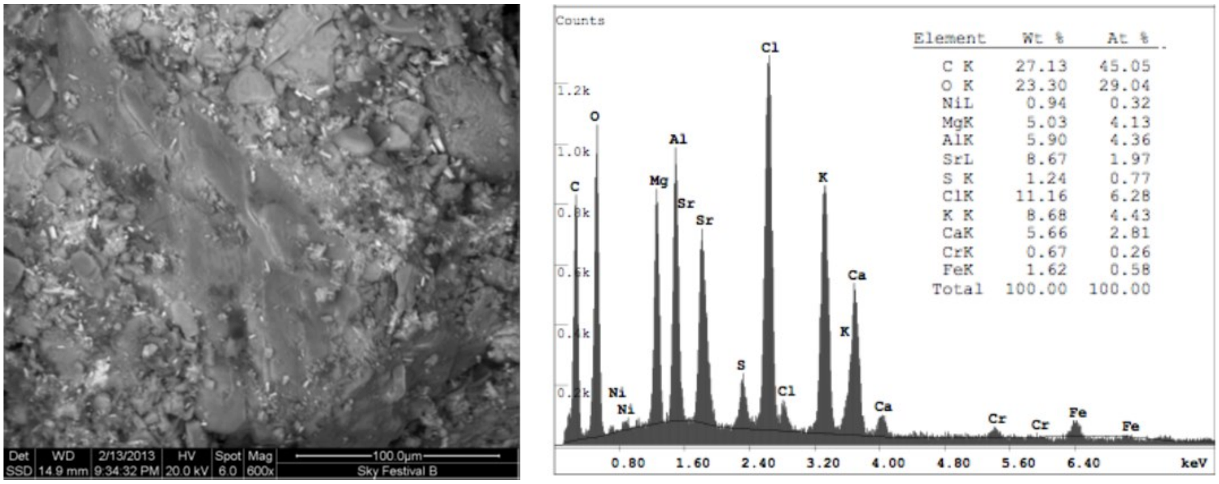


Figure 22. SEM and EDAX data for Sky Festival B sample.

Data Summary of Sky Festival B:

Mechanical Insult Data

- Impact (H50%) – 14 cm
- Friction (F50%) – 15 psi
- ESD (Joules) – 0.025 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K, Sr and Ca
- Predominant metals (ICP-AES) – Mg, Al, K, Sr and Ca
- Anion(s) – perchlorate
- Other species – sulfur (1.2%/wt)

Thermal Sensitivity Data

- DSC exotherm – NA
- Other DSC features – endotherm and subsequent perturbation at and above 305 °C probably indicates a $KClO_4$ crystal phase transition.

5.2.3. Sky Festival Sub-sample C

4.679 g of this material was delivered. This sample is a fine silvery powder, as shown in Figure 23. SEM and EDAX data are shown in Figure 24. The X-ray data shown represents the entire SEM image. The white particle in the box is nearly pure titanium, and the grayish particle is nearly completely aluminum.

Figure 23. Enlargement of photo of Sky Festival Sub-sample C.

X-ray analysis indicates that the material is composed of magnesium and aluminum, potassium and chlorine. Small quantities of titanium are also present. There is no sulfur in this sample, and LC/MS and FTIR show that the chlorine is present as the perchlorate anion. This sample is appreciably less sensitive to initiation by impact than many of the other flash powder-like samples, perhaps because of the lack of sensitization by sulfur.

DSC results indicate that this sample does not decompose at temperatures less than 500 °C.

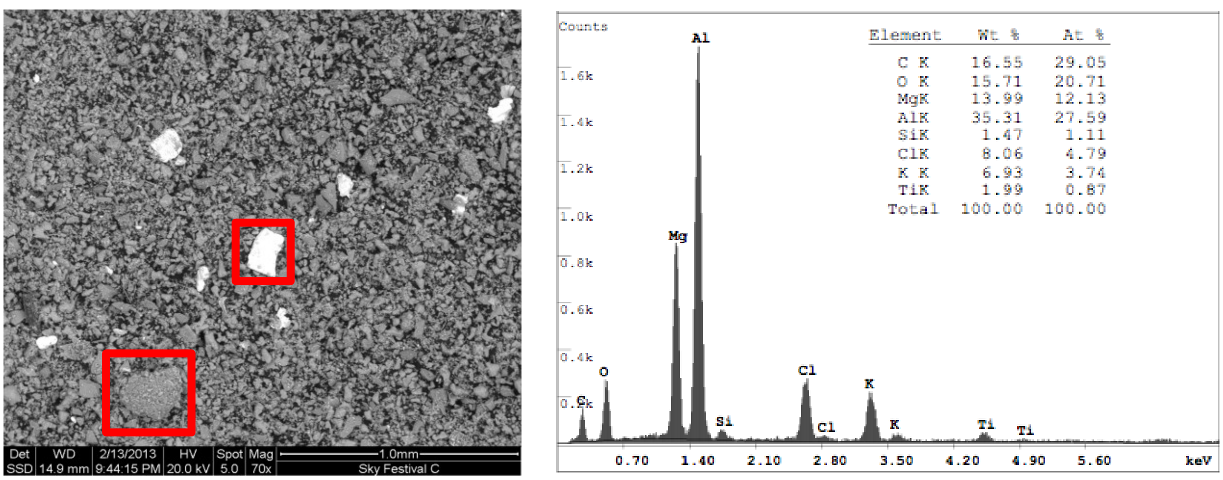


Figure 24. The EDAX analysis on this slide is of the whole image.

Data Summary of Sky Festival C:

Mechanical Insult Data

- Impact ($H_{50\%}$) – Initiation not observed.
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.025 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K

- Predominant metals (ICP-AES) – Mg, Al, K
- Anion(s) – perchlorate
- Other species – NA

Thermal Sensitivity Data

- DSC exotherm – NA
- Other DSC features – endotherm at 305 °C indicates a $KClO_4$ crystal phase transition.

5.2.4. Sky Festival Sub-sample D

This sample is another fine grayish powder, as shown in Figure 25. 5.063 g of this material was delivered. The SEM-EDAX data (Figure 26) of this sample shows a similar composition to Sky Festival C, except that one of the larger particles interrogated by the x-rays contains a large concentration of phosphorus. This signal is quite localized, not being visible in the x-ray signatures of the sample as a whole, and entirely missing from the ICP data. Potassium, aluminum and magnesium are present in large concentrations. This sample has a wide array of cations present in minor quantities, including calcium, silicon and iron. The only anion present in appreciable quantities is perchlorate, as reported by both FTIR and IC/MS.

DSC results indicate that this sample does not decompose at temperatures less than 500 °C.

Figure 25. Enlarged photo of Sky Festival sample D.

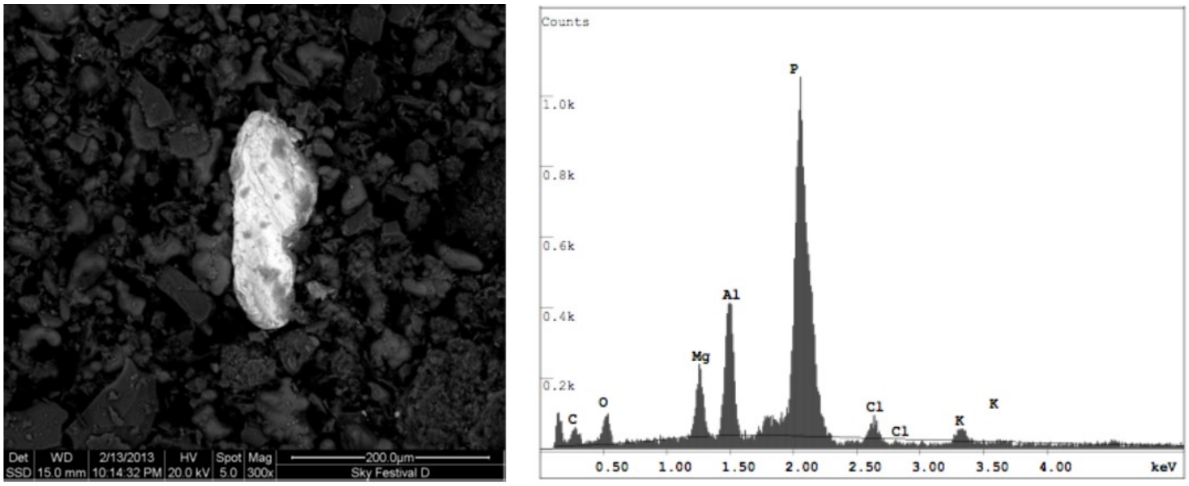


Figure 26. SEM and EDAX data on Sky Festival D, note the predominance of the P peak.

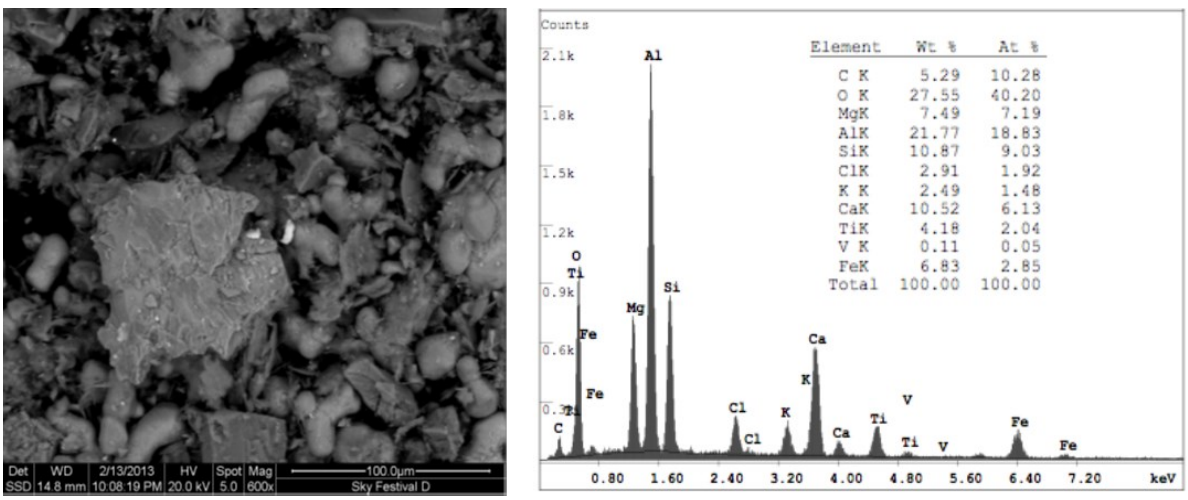


Figure 27. SEM and EDAX data on Sky Festival D.

Data Summary of Sky Festival D:

Mechanical Insult Data

- Impact ($H_{50\%}$) – Initiation not observed.
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.025 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K, Ca, Si, Fe
- Predominant metals (ICP-AES) – Mg, Al, K, Ca, Si, Fe
- Anion(s) – perchlorate
- Other species – P

Thermal Sensitivity Data

- DSC exotherm – NA
- Other DSC features – endotherm at 305 °C indicates a $KClO_4$ crystal phase transition.

5.2.5. Sky Festival Sub-sample E

1.181 g of this sample was received. The sample is composed of coarse black particles, about 0.5 mm across. This material has x-ray signatures associated with black powder, potassium and sulfur dominating. Insufficient sample quantity was delivered to perform all analyses on this sample, but it was submitted to SEM-EDAX, chromatography and mechanical insult testing.

Figure 28. Enlarged photo of Sky Festival E

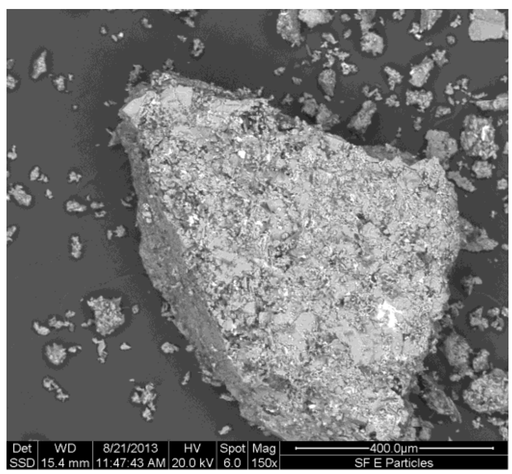


Figure 29. SEM image of Sky Festival E, scale on bottom

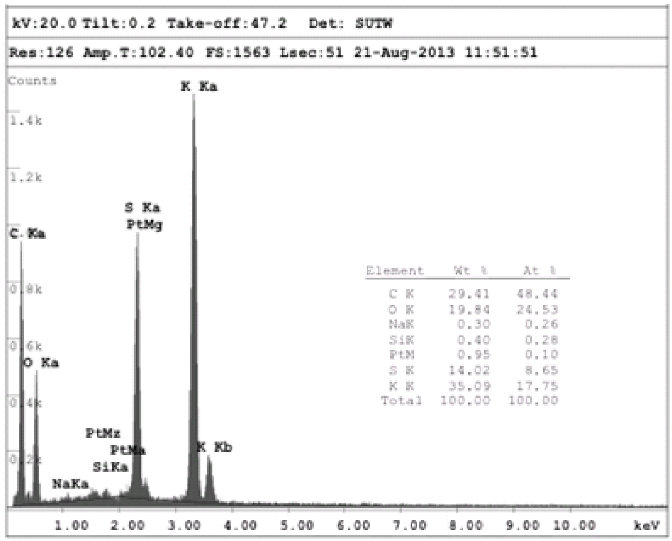


Figure 30. EDAX results of Sky Festival E, S and K dominating

Data Summary of Sky Festival E:

Mechanical Insult Data

- Impact ($H_{50\%}$) – Initiation not observed.
- Friction ($F_{50\%}$) – Initiation not observed.
- ESD (Joules) – 0.63 J

Primary Chemical Results

- Predominant metals (EDAX) – K and small amounts of other materials
- Predominant metals (ICP-AES) – Not performed
- Anion(s) – nitrate only
- Other species – S (14%/wt)

Thermal Sensitivity Data

- DSC exotherm – not performed
- Other DSC features – not performed

5.2.6. Sky Festival Sub-sample F

0.714 g of this material was delivered. This was a generally copper colored powder with some black particles present. Elementally, the particles show a fairly homogenous make-up. Again, the powder was course grained, as shown in Figure 31. EDS shows the black particles as predominantly Si and Al, with Fe present, as shown in Figure 30. The copper colored particles have a similar elemental make-up. The use of the carbon tape to secure the samples to the stage in the instrument makes the C and O signals difficult to interpret, but judging from the rest of the x-ray data, this material is an alumino-silicate clay, sometimes used for creating gas nozzles and separating stages from one another. Due to the very small quantity of material received, only peremptory mechanical insult testing was done. There appeared to be no sensitivity to any stimulus in these tests. Anion analysis yielded a nitrate signal only.

Figure 31. Enlarged photo of Sky Festival F

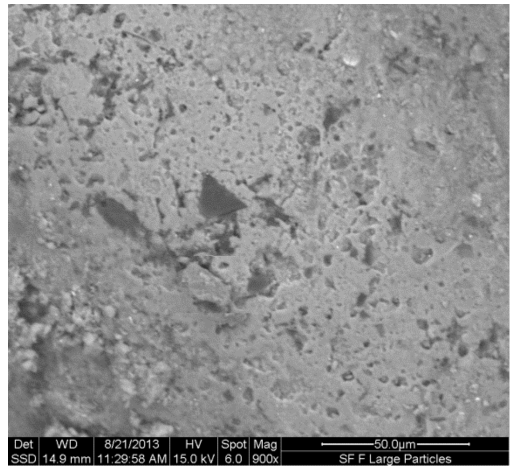


Figure 32. SEM image of Sky Festival F, showing texture of black particle

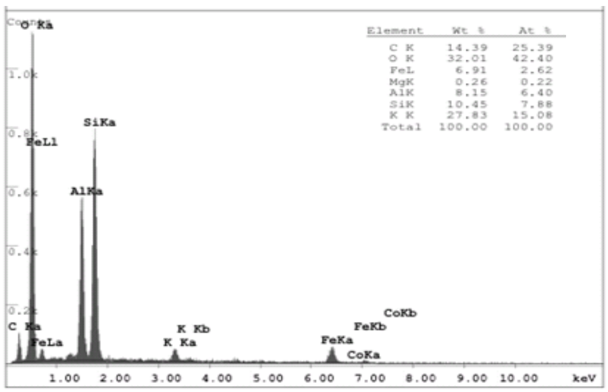


Figure 33. EDAX results of Sky Festival F, showing a clay-like composition

Data Summary of Sky Festival F:

Mechanical Insult Data

- Impact ($H_{50\%}$) – TIL not tested, appears to be unreactive
- Friction ($F_{50\%}$) – TIL not tested, appears to be unreactive
- ESD (Joules) – Not tested.

Primary Chemical Results

- Predominant metals (EDAX) – Al and Si, Fe, small amounts of K
- Predominant metals (ICP-AES) – Not performed
- Anion(s) – nitrate only
- Other species – NA

Thermal Sensitivity Data

- DSC exotherm – not performed
- Other DSC features – not performed

5.2.7. Sky Festival Sub-sample G

This was a grayish, course grained powder (Figure 34 and Figure 35). EDAX composition shows the presence of S, Al, Mg and Sr, as shown in x-ray spectra presented in Figure 36. 1.858 g of this material was received. "Small 'Comet' Tube Lift Charge Sample" was written on the sample bag. The material as delivered had two pieces of fusing in it. This material was received also in very small quantity, so SEM-EDAX, chromatography and mechanical insult were the only tests performed on this material.

Figure 34. Photo of Sky Festival G sample

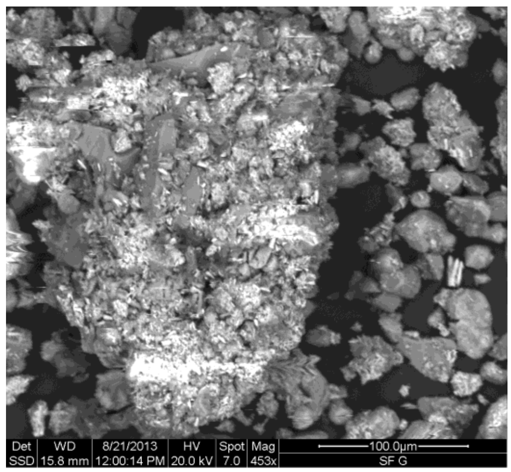
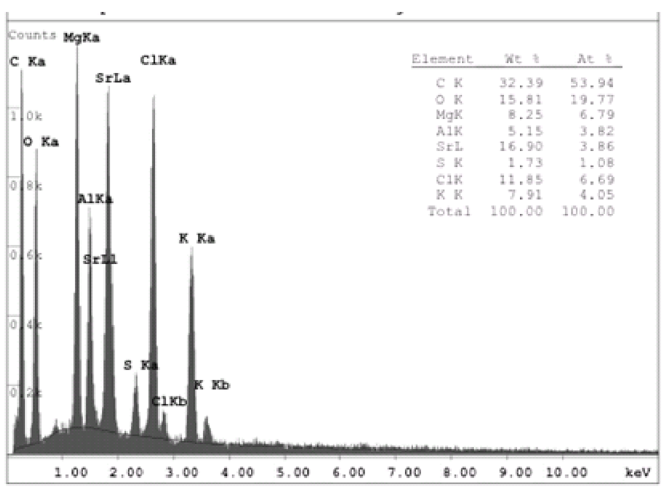


Figure 35. SEM image of Sky Festival G sample



Element	Wt %	At %
C K	32.39	53.94
O K	15.81	19.77
MgK	8.25	6.79
AlK	5.15	3.82
SrL	16.90	3.86
S K	1.73	1.08
ClK	11.85	6.69
K K	7.91	4.05
Total	100.00	100.00

Figure 36. EDAX results of Sky Festival G sample

Data Summary of Sky Festival G:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 20 cm
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.25 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K, and Sr
- Predominant metals (ICP-AES) – not performed
- Anion(s) – perchlorate
- Other species – sulfur (1.7%/wt)

Thermal Sensitivity Data

- DSC – not performed

5.3 Halawa Samples

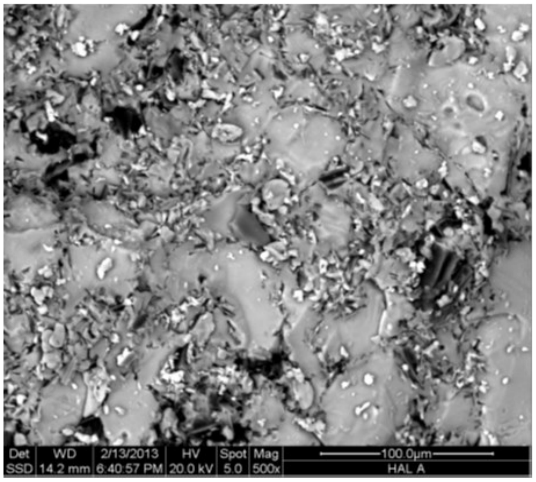
5.3.1. Halawa Sample A

This sample is composed of black pebbles, with brown granules. 6.680 g of this material was received, “Lift charge” was written on the sample bag. It is similar in appearance to the O Triple C B sample, save that it contains no fuse-type material. Figure 37 contains an enlarged photo of the sample in a Velostat container.

Figure 37. Enlarged photo of Halawa sample A.

SEM and EDAX data for this sample is shown in Figure 38 which is dominated by potassium and sulfur signals. Chlorine is completely absent from the X-ray data. ICP analysis verifies the dominance of K and S, and also the lack of aluminum and magnesium. The sole anion identified by both FTIR and IC/MS is nitrate.

DSC results indicate that this sample begins to decompose when heated past 363 °C



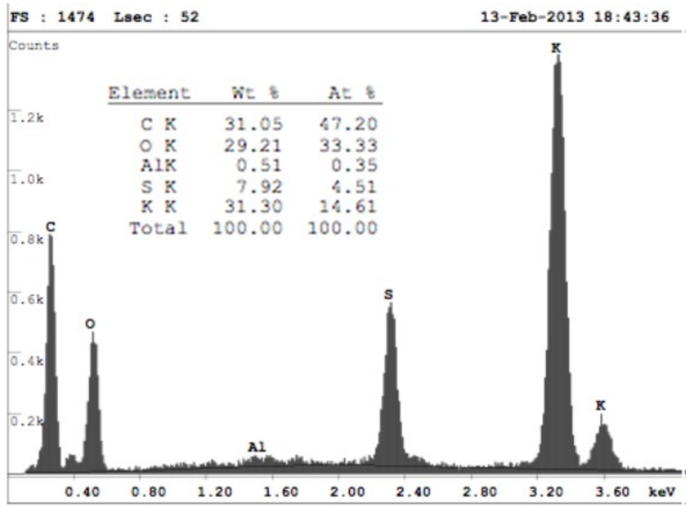


Figure 38. SEM and EDAX data for Halawa sample A.

Data Summary of Halawa A:

Mechanical Insult Data

- Impact ($H_{50\%}$) – Initiation not observed
- Friction ($F_{50\%}$) – Initiation not observed
- ESD (Joules) – 0.063 J

Primary Chemical Results

- Predominant metals (EDAX) – K
- Predominant metals (ICP-AES) – K
- Anion(s) – nitrate
- Other species – S (8%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 363 and peaking at 433 °C is indicative of decomposition
- Other DSC features – endotherm at 134 °C is likely the KNO_3 (α to β) crystalline phase change. The endotherm at 332 °C is KNO_3 melting.

5.3.2. Halawa Sample B

This sample is a fine gray powder containing larger gray chunks. 5.656 g of this material was received. An enlarged photograph of the sample in a Velostat container is shown in Figure 39. The chunks in this material are not as regular as in other similar samples. The SEM and EDAX data for this material is shown in Figure 40, which has an x-ray spectrum similar to that of the other flash powder samples, consisting of powdered aluminum and magnesium, chlorine and potassium and titanium. There is also a smaller concentration of silicon. These materials are also identified in the ICP data. The sole anion identified by both LC/MS and FTIR is perchlorate.

DSC results indicate that this sample does not decompose at temperatures less than 500 °C.

Figure 39. Enlarged photo of Halawa sample B

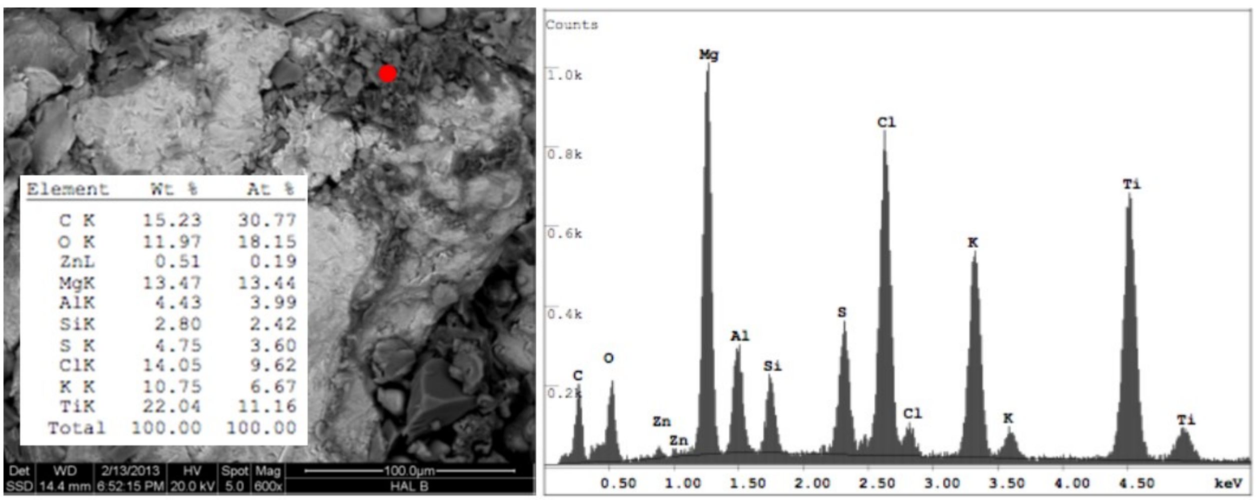


Figure 40. SEM and EDAX data for Halawa sample B

Data Summary of Halawa B:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 50 cm
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.013 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, S, K, Ti, Si
- Predominant metals (ICP-AES) – Mg, Al, K, Ti, Si
- Anion(s) – perchlorate

- Other species – S (2.4%/wt)

Thermal Sensitivity Data

- DSC exotherm – NA
- Other DSC features – endotherm at 113 °C is likely loss of moisture, at 305 °C, the endotherm is likely $KClO_4$ phase transition.

5.3.3. Halawa Sample C

This sample is another finely divided gray powder. 5.706 g of this material was received. A photo is provided in Figure 41. SEM and EDAX data is presented in Figure 42. The x-ray spectrum is very similar to the preceding sample, showing high concentrations of magnesium and aluminum, sulfur and chlorine. There are smaller amounts of potassium and titanium. These results are corroborated by the ICP analysis except that the sulfur is not seen in those data (the detection limits for S in ICP are quite high, so this is not a concern). The only anion observed in the data in any abundance is perchlorate.

This sample is quite heterogeneous, which is related to the wide range of sulfur measurements received in EDAX results. There was no "large area" EDAX taken for this particular sample, and therefore the range of the sulfur results is reported, rather than one that is representative of the sample as a whole.

DSC results indicate that this sample does not decompose at temperatures less than 500 °C.

Figure 41. Enlarged photo of Halawa C sample.

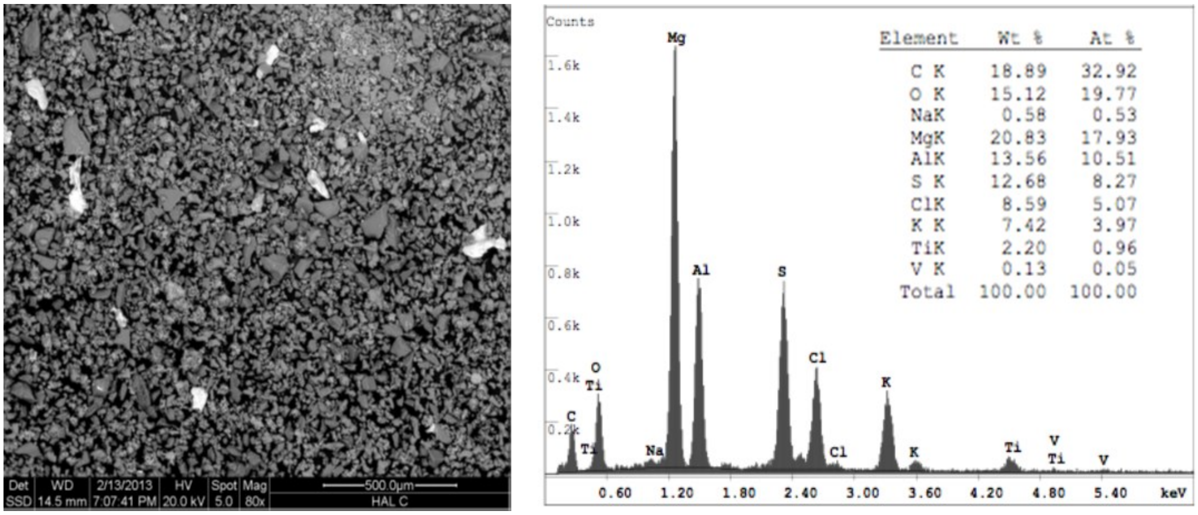


Figure 42. SEM and EDAX data for Halawa C sample.

Data Summary of Halawa C:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 72 cm
- Friction ($F_{50\%}$) – 9 psi
- ESD (Joules) – 0.063 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K, Ti
- Predominant metals (ICP-AES) – Mg, Al, K, Ti
- Anion(s) – perchlorate
- Other species – sulfur (4-13%/wt)

Thermal Sensitivity Data

- DSC exotherm – NA
- Other DSC features – endotherm at 113 °C is either loss of moisture or melting of the small amount of sulfur in the sample. The endotherm at 305 °C, the endotherm is likely $KClO_4$ phase transition.

5.4 Krazy Kids Samples

5.4.1. Krazy Kids Sample A

This sample is shown in an enlarged optical photograph in Figure 43. 8.178 g of this material was received, written on the sample bag were the words "Lift, 2 Charges BSP." It has the overall appearance of lift charge material, "black powder," and there were pieces of fuse material delivered with the sample. SEM (Figure 44) shows it to be composed of very large particles, and

EDAX taken across the entire field of view demonstrates that it is free of any chlorine compound, a result that is mirrored in both the FTIR and the anion (IC) analytical data. Instead, this sample contains nitrate, which is most likely the counter-ion to the potassium, and sulfur. ICP analysis verifies the presence of the potassium and the absence of any meaningful amount of any other metals. X-ray data indicates a small quantity of aluminum, possibly a local contaminant, since the ICP-OES analysis does not contain Al signals.

DSC results indicate that this sample decomposes when heated above 363 °C.

Figure 43. Enlarged photo of Krazy Kids sample A.

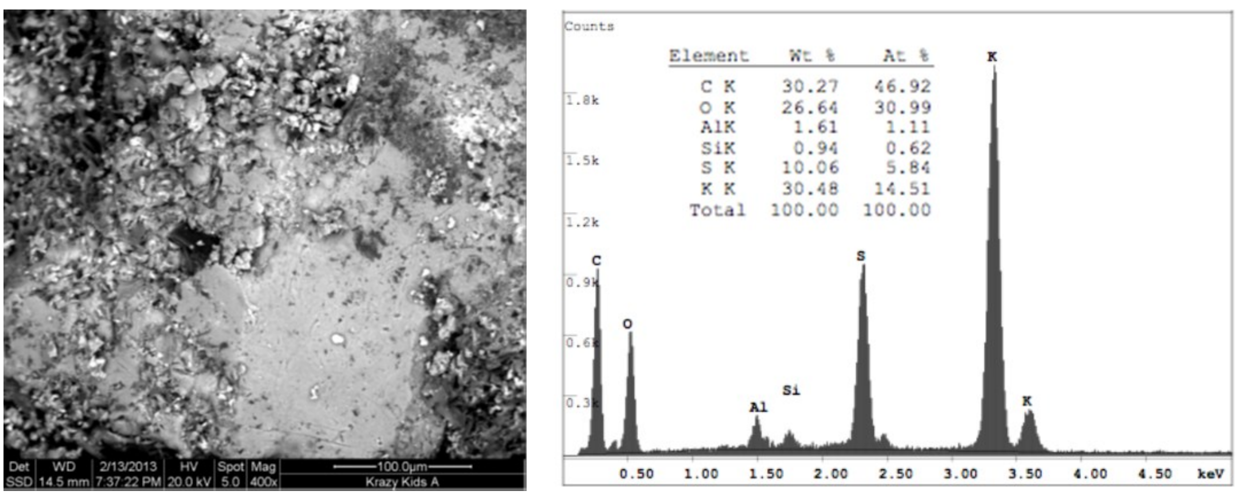


Figure 44. SEM and EDAX data of Krazy Kids sample A.

Data Summary of Krazy Kids A:

Mechanical Insult Data

- Impact ($H_{50\%}$) – Initiation not observed
- Friction ($F_{50\%}$) – Initiation not observed
- ESD (Joules) – 0.25 J

Primary Chemical Results

- Predominant metals (EDAX) – K, small peak associated with Al
- Predominant metals (ICP-AES) – K
- Anion(s) – nitrate
- Other species – sulfur (10%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 363 and peaking at 429 °C is indicative of decomposition; the appearance of an exotherm at 321 °C in one test has not been identified.
- Other DSC features – endotherm at 134 °C is likely the KNO_3 (α to β) crystalline phase change. The endotherm at 332 °C is KNO_3 melting.

5.4.2. Krazy Kids Sample B

11.248 g of this sample was received. This sample is composed of a silvery gray powder and cylindrical gray pellets about 1 cm tall x 0.75 cm wide. Figure 45 is an enlarged optical photograph of the sample material in a Velostat container. The larger roundish particles were cut into powder with a razor blade at the time of the mechanical insult testing, and this prepared sampled was used to acquire SEM and EDAX data (Figure 46).

Figure 45. Enlarged photo of Krazy Kids sample B.

The SEM and EDAX data show small peaks associated with aluminum and magnesium, larger ones that are characteristic of potassium and sulfur, and several features related to barium, an element usually used to create color in pyrotechnics. The barium signals are related to the white speckles in the SEM image, the darker material is devoid of this element, and the sulfur and potassium features dominate. This sample is unique in the test set in that there are two anionic species associated with it, nitrate and perchlorate. This is less obvious in the FTIR data than the aqueous laboratory work-up.

DSC results indicate that this sample decomposes when heated above 354 °C.

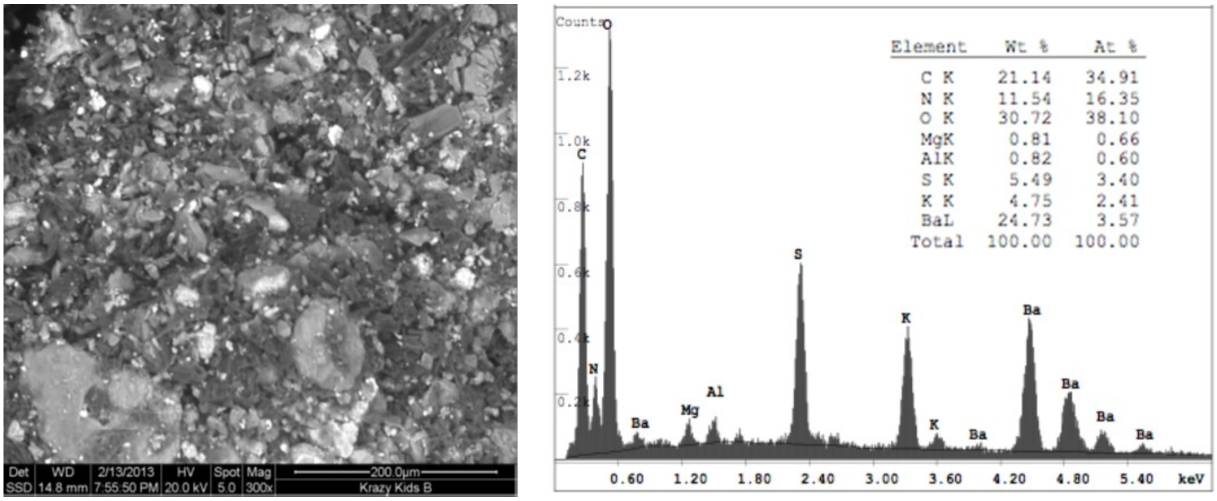


Figure 46. SEM and EDAX data of white regions of Krazy Kids sample B, Ba peaks dominating.

As we discussed in the initial description of samples, many star and comet recipes available on the internet have both nitrate and perchlorate in them.

Data Summary of Krazy Kids B:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 28 cm
- Friction ($F_{50\%}$) – 265 psi
- ESD (Joules) – 0.063 J

Primary Chemical Results

- Predominant metals (EDAX) – K, small peak associated with Al, lots of Ba
- Predominant metals (ICP-AES) – K, Al (looks higher in the ICP than the EDAX), lots of Ba
- Anion(s) – nitrate and perchlorate
- Other species – S (12%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 354 and peaking at 439 °C is indicative of decomposition.
- Other DSC features – endotherm at 113 °C is either loss of moisture or melting of the small amount of sulfur in the sample. The endotherm at 320 °C is likely $KClO_4$ phase transition.

5.4.3. Krazy Kids Sample C

11.293 g of this sample was received. This sample is composed of grayish powder and larger gray chunks. This sample is composed of a silvery gray powder and cylindrical gray pellets about the twice the size of BBs (dimensions approximately 1 cm tall x 0.75 cm wide). Figure 47 is an enlarged optical photograph of the sample material in a Velostat container. The larger cylindrical-shaped particles were cut into powder with a razor blade at the time of the mechanical insult testing, and this prepared sampled was used to acquire SEM and EDAX data (Figure 48).

Figure 47. Enlarged photo of Krazy Kids sample C.

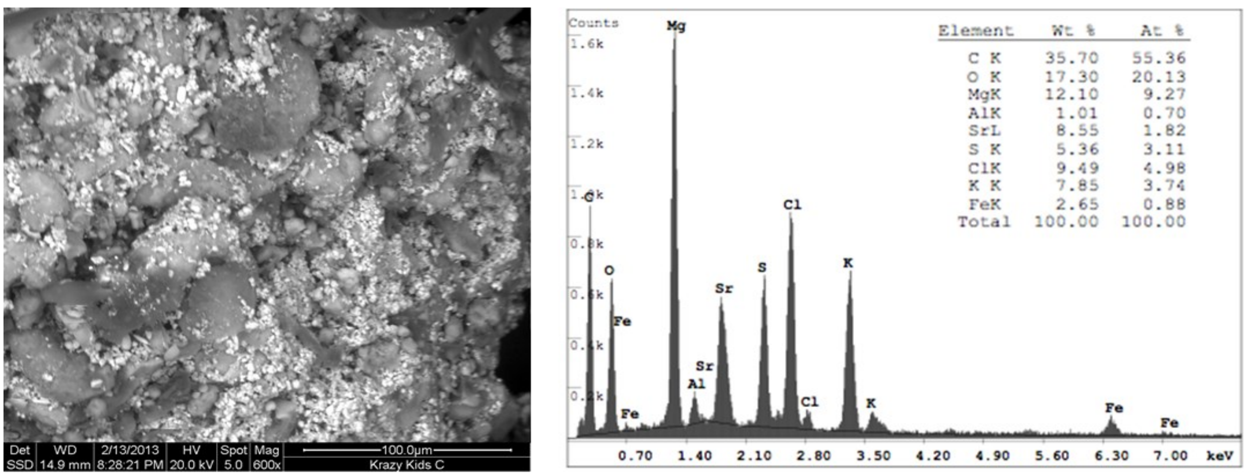


Figure 48. SEM and EDAX data of Krazy Kids sample C.

X-ray data from this sample indicates classic flash powder components with strontium used as a colorant. ICP-AES corroborates the presence of aluminum, calcium, potassium, magnesium, sulfur and strontium. FTIR shows both nitrate and perchlorate, in agreement with LC/MS.

DSC results indicate that this sample decomposes when heated above 353 °C.

Data Summary of Krazy Kids C:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 23 cm
- Friction ($F_{50\%}$) – 134 psi
- ESD (Joules) – 0.13 J

Primary Chemical Results

- Predominant metals (EDAX) – Mg, Al, K, Sr

- Predominant metals (ICP-AES) – Mg, Al, K, Sr, Ca
- Anion(s) – nitrate and perchlorate
- Other species – sulfur (7%/wt)

Thermal Sensitivity Data

- DSC exotherm with onset at 353 and peaking at 439 °C is indicative of decomposition. The small exotherm peaking at 300 °C in one test has not yet been identified.
- Other DSC features – endotherm at 116 °C is either loss of moisture or melting of the small amount of sulfur in the sample. The endotherm at 300 °C is likely $KClO_4$ phase transition.

5.5 Standards

5.5.1. Potassium chlorate and aluminum homemade flash powder

This standard was made by mixing 1.38 grams of atomized aluminum powder with 0.62 grams of potassium chlorate. The two components were mixed by hand for approximately 10 minutes before being submitted to testing.

Data Summary of $KClO_3$ and Al standard:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 71 cm
- Friction ($F_{50\%}$) – 71 psi
- ESD (Joules) – 0.013 J

Primary Chemical Results

- Predominant metals (EDAX) –Al, K, Cl
- Predominant metals (ICP-AES) – Al and K
- Anion(s) – chlorate and perchlorate, some question about the purity of this standard. Discussions with Test America yielded no particular reason that a sample that had been produced with only potassium chlorate and aluminum powder could result in a significant perchlorate signal.
- Other species – NA

Figure 49. $KClO_3$ crystal in homemade flash powder

Element	Wt %	At %
C K	30.31	49.20
O K	16.92	20.62
AlK	12.65	9.14
ClK	20.27	11.15
K K	19.84	9.89
Total	100.00	100.00

Figure 50. EDAX results for $KClO_3$ flash powder

5.5.2. Potassium perchlorate and aluminum homemade flash powder

This standard was made by mixing 1.36 grams of atomized aluminum powder with 0.64 grams of potassium perchlorate. The two components were mixed by hand for approximately 10 minutes before being submitted to testing.

Data Summary of $KClO_4$ and Al standard:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 60 cm
- Friction ($F_{50\%}$) – 77 psi
- ESD (Joules) – 0.013 J

Primary Chemical Results

- Predominant metals (EDAX) – Al, K, Cl
- Predominant metals (ICP-AES) – Al and K
- Anion(s) – perchlorate, very small chlorate signature
- Other species – NA

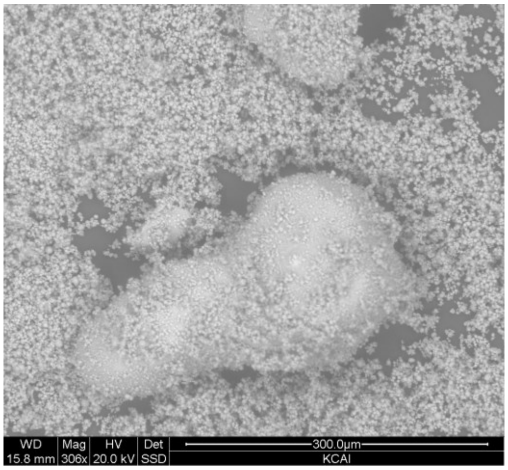


Figure 51. SEM of $KClO_4$ and Al flash powder standard

Element	Wt %	At %
C K	19.82	37.12
O K	7.17	10.08
AlK	37.63	31.38
ClK	18.00	11.42
K K	17.38	10.00
Total	100.00	100.00

Figure 52. EDAX results from $KClO_4$ and Al flash powder

5.5.3. Potassium perchlorate/chlorate mixed and aluminum homemade flash powder

This standard was made by mixing 0.63 grams of atomized aluminum powder with 0.685 grams of potassium perchlorate and 0.685 g of potassium chlorate. The three components were mixed by hand for approximately 10 minutes before being submitted to testing.

DSC results indicate that this sample does not decompose at temperatures less than 500 °C.

Data Summary of $KClO_3$/$KClO_4$ and Al standard:

Mechanical Insult Data

- Impact ($H_{50\%}$) – 55 cm
- Friction ($F_{50\%}$) – 77 psi
- ESD (Joules) – 0.013 J

Primary Chemical Results

- Predominant metals (EDAX) –Al, K, Cl
- Predominant metals (ICP-AES) – Al and K
- Anion(s) –perchlorate and chlorate
- Other species – NA

Thermal Sensitivity Data

- DSC exotherm - NA
- Other DSC features –endotherms at 305 and 358 °C are likely $KClO_4$ phase transition and the melting of the $KClO_3$ in the sample, respectively. **This result suggests that DSC alone can be utilized to determine the presence of chlorate in fireworks samples that decompose at temperatures higher than its melting point.**

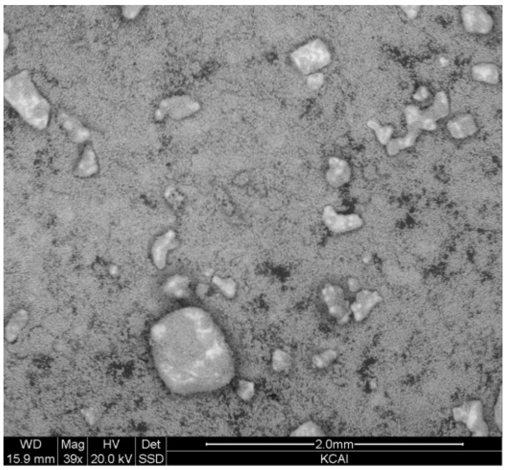


Figure 53. SEM image of KP&KC + Al homemade flash powder

Element	Wt %	At %
C K	4.54	9.59
O K	1.81	2.86
AlK	91.64	86.17
ClK	1.05	0.75
K K	0.97	0.63
Total	100.00	100.00

Figure 54. EDAX analysis of the mixed flash powder

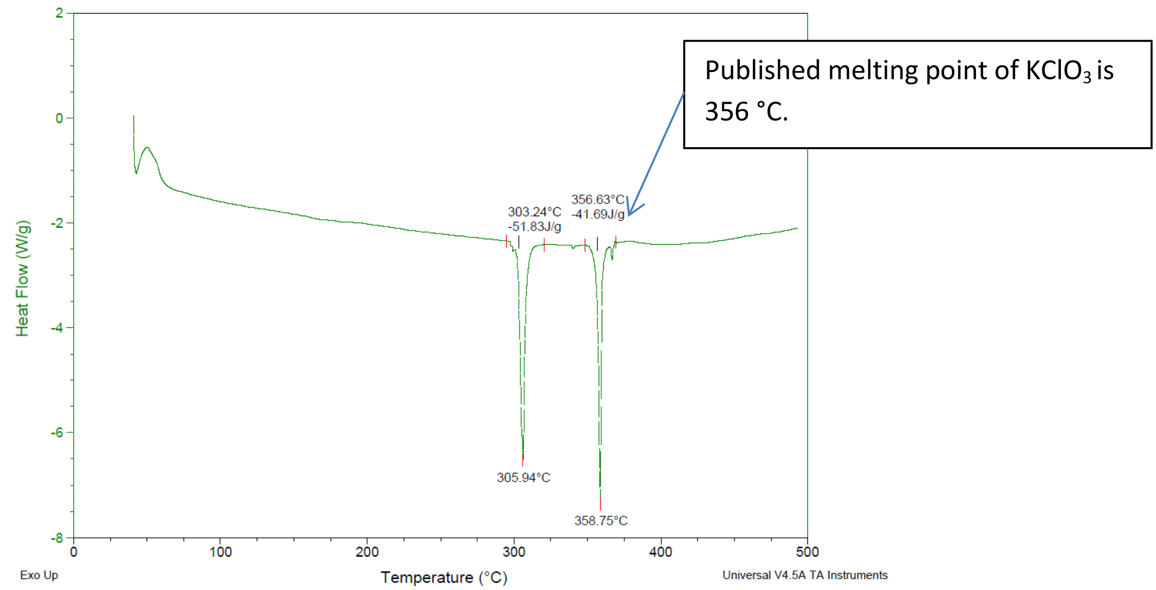


Figure 55. DSC run of mixed flash powder, showing that chlorate can be detected in a DSC endotherm

6.0 Discussion

In this section, items not fully addressed in sections related to individual materials are discussed. These issues include the categories into which the materials fall by virtue of chemical and physical characteristics, some commentary on particle size and a brief note about endothermic data in DSC test results.

6.1 Results Categorization

Major results of this testing program are presented in Tables 2 and 3. Overall, the results of the chemical, thermal and mechanical insult testing of the materials fell naturally into three classes of explosive materials, and one sample of non-explosive material (See Table 3):

- Lift Charges
- Flash Powder
- Stars/Comets
- Clay

The results demonstrate how chemical and physical properties of the various sections within the fireworks are conserved.

6.1.1 Lift Charges

Lift charge materials, with physical descriptions of "black pebbles" and the like, contain relatively high concentrations of sulfur (around 10%/wt) and large concentrations of KNO_3. They all exhibit thermal decomposition events that show onset around 360 °C and peak at about 440 °C. They are sensitive to electrostatic discharge, but not impact or friction, and contain potassium and nitrate anions. The decomposition (ignition) temperature and overall lack of sensitivity to mechanical forces matches those in the literature well.[8]

6.1.2 Flash Powder

The second clear category is flash powder material with a relatively low sulfur content (in general, <3%/wt). These materials are more sensitive to friction and ESD than PETN and RDX, and therefore to be classed as primary explosive materials, but less sensitive to impact than these standards. All samples contain high concentrations of both Al and Mg, and perchlorate. Very small chlorate signals are seen in some materials, but all represent overall chlorate concentrations of <0.1%/wt. These materials do not thermally decompose at temperatures less than 500 °C, further indicating negligable chlorate concentration. The high decomposition (ignition) temperature has been documented in the case of flash powder materials containing magnesium. The chemical components of these materials and sensitivity to mechanical forces match those in the literature well.[8]

6.1.3 Stars/Comets

"Stars" or "comets" are larger particle size materials with a higher sulfur content. Most of these materials are quite sensitive to reaction after mechanical stress, and are also sensitive to ESD. Because of this sensitivity, these materials should also be considered primary explosives. As a class, they have more variability than the other two classes of results. In general, they have higher concentration of sulfur than the flash powder samples. They also have higher concentrations of salts related to color production in the device, only some of these materials contain nitrate. All samples contain large concentrations of perchlorate. Very small chlorate signals are seen in some materials, but all represent overall chlorate concentrations of <0.1%/wt. Decomposition at high temperatures happens in all samples, but under conditions that vary appreciably, instead of the relatively conserved behavior of the lift charge samples. In these samples, the onset of the exotherm is around 350 °C, and reaches its peak at 400-450 °C, roughly matching the ignition temperatures listed in Conkling for a flash powder recipe containing sulfur.[8]

6.1.4 Clay

The last sample, Sky Festival #F, appears to be pyrotechnic clay, as the primary elements found within are aluminum and silicon. This sample was not fully tested, as a very small quantity was received, but informal mechanical insult testing shows it to be insensitive.

6.2 Particle Size Effects

For a given material, the level of insult required to initiate a reaction, and the subsequent extent of that reaction in any of these tests is not only a function of its basic chemical composition, but its physical characteristics as well. These physical characteristics include physical state (i.e., gas, liquid or solid), and in the case of solids in particular, compacted samples versus particulates or powders, and the particle size of those powders. Almost all commercial propellants and pyrotechnics are produced and packaged in powder form, although the particle sizes of those powders can vary significantly. Their reaction rates are a function of both pressure and of particle size: as pressure increases, the burn rate will increase and for a specific material at a fixed pressure, smaller grain powders will burn faster than larger grain powders. Likewise, a specific material will typically exhibit greater sensitivity to thermal insults, whether internally generated or from external heat sources, as the particle size is decreased.

In the present results, there are notable differences in particle size (documented in SEM images), however, no analysis was performed upon this aspect of the sample. This is chiefly due to the presence of chemical variability that would serve to make unequivocal designation of particle size effects difficult and uncertain.

6.3 Differential Scanning Calorimetry Observations

Differential scanning calorimetry (DSC) was performed on all but the Sky Festival samples #E, #F and #G. The DSC provides two principal types of information, the presence or absence of a decomposition exotherm, which has already been discussed. The second type of information is based on the interpretations of the endotherms which exist prior to any decomposition event. It is clear throughout the data that the presence and temperatures of these endotherms can help to identify fireworks components. For example, crystal rearrangement and melting of KNO_3 were visible in the DSC data of the lift charges. The consistency of the temperature of all the decomposition exotherms present in this data set may well be related to the boiling point of sulfur at 445 °C and the substantial vapor pressure developed before reaching the actual boiling temperature. The most interesting thing about the endotherms are their probable use in distinguing the presence of substantial concentrations of pyrotechnically interesting salts based on melting or crystal rearrangement points.

The chemical formulations that are intimated by the testing are all quite ordinary, being discussed at length in both internet resources and hardcopy ones, with one exception.[7,8] Sky Festival #D sample exhibited one particle with a significant phosphorus signature when probed by a very narrow excitation beam in EDAX. This signal is not repeated in either the less focused EDAX nor in the ICP data. In fact, of the five EDAX spectra collected on this particular sample, there is a phosphorus signature in only one, indicating a low overall concentration of this element in the material. This sample is not more sensitive than the other flash powder type materials, either on a mechanical or thermal basis, so this result, although interesting, in all likelihood does not represent a substantial deviation from the compositions of the other samples in the tested set.

7.0 Conclusion

Analysis of Pyrotechnic Components results indicate that the test samples provided behaved in ways that are consistent with extant fireworks literature available both in internet and hardcopy resources. Flash powders and their derivatives are recognized as extremely dangerous materials that are very sensitive to ignition by common handling forces, including impact, friction and static discharges of the magnitude possible from the human body. This high level of sensitivity is the rationale behind safety warnings and precautionary advice given in every guide to handling these compounds. These warnings include remote mixing of larger quantities and advice not to store bulk flash powder near personnel.

8.0 References

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9. 0 Appendix

To be submitted separately on a CD. Many of the raw data sets are very large files.

10.0 Acknowledgments

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