Black Powder, Black Powder Substitutes, and Pyrotechnics Analysis

1 Scope

These procedures describe the general process for the analysis of bulk black powder, black powder substitutes, and pyrotechnics (such as fireworks, flash powder, and flares) and the identification of their components. These procedures are suitable for bulk samples which are suspected of being a black powder, black powder substitute, or pyrotechnic. These procedures apply to caseworking personnel conducting work in explosives chemistry analysis.

2 Introduction

Black powder and black powder substitutes are classified as low explosive propellants. Black powder is commonly used as a propellant in muzzle loading firearms, in pyrotechnics, in blasting, and in fuses.

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A pyrotechnic is a mixture of chemical elements and compounds that is capable of a self-contained and self-sustained exothermic chemical reaction, for the production of heat, light, gas, smoke, or sound. Pyrotechnics may include fireworks, flash powders, smoke grenades, thermites, matches, and flares. Pyrotechnics must contain at least one fuel and oxidizer.

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Flash powder is generally gray or metallic in color varying from a visibly homogeneous mixture to a granular heterogeneous mixture. Redacted It will produce a bright flash upon initiation with a flame.

A flare or fusee contains a pyrotechnic material designed to produce a single source of intense light, heat, or radiation for certain durations and can be used for signaling, as a source of ignition, or for other purposes. It is generally composed of a match head, striker, and a pyrotechnic material.

Table 1 contains example compositions of black powder, black powder substitutes, and pyrotechnics.

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3 Equipment/Materials/Reagents

Equivalent equipment, materials, and reagents may be substituted as needed.

3.1 Equipment

- Balance
- Fourier transform infrared (FTIR) spectrometer with attenuated total

reflectance (ATR) or microscope attachment
- Gas chromatograph with flame ionization detector (GC/FID)
- Gas chromatograph with mass spectrometer (GC/MS)
- Ion chromatograph (IC)
- Microscope (optical or digital)
- Raman spectrometer with macro compartment or microscope attachment
- Scanning electron microscope with energy dispersive X-ray spectrometer (SEM/EDS)
- Solids probe mass spectrometer/mass spectrometer (MS/MS)
- X-ray diffractometer (XRD)

3.2 Materials

- Aluminum or copper tape
- Autosampler vials and caps
- Disposable plastic syringes
- Forceps
- Kraft paper
- Lighter, torch, or matches
- Mortar and pestle
- Scalpel
- SEM stubs or carbon planchets with liquid adhesive (e.g., Duro-tak), carbon adhesive tabs, or aluminum or copper tape
- Solids probe cups
- Spatula
- Syringe filters (0.2 µm nylon filter)
- Various disposable glassware and plasticware
- XRD sample holders (zero background holder with or without depression)

3.3 Reagents/Solvents/Reference Materials

- Deionized water (18.2 MΩ)
- Hexane (reagent grade)
- Isopropyl alcohol (70% commercial product)
- Methanol (HPLC grade)

4 Standards and Controls

All reference materials and reagents will be verified prior to, or in concurrence with, use in casework. Refer to the Verification of Reagents and Solvents Standard Operating Procedure (SOP), the Verification of Reference Materials SOP, and the Records of Items Used As Known Materials SOP. Refer to the Instrument Parameters and Reagent Preparation SOP for

information regarding the components and preparation of all standards and controls referred to in this document.

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4.1 Black Powder or Black Powder Substitute Positive Control

A positive control of black powder or black powder substitute will be prepared in a manner appropriate for the analytical technique being used.

4.2 Fuel Oil Positive Control

The fuel oil positive control is a 500 ppm solution of fuel oil #2 in an appropriate solvent (e.g., methanol, hexane, or carbon disulfide).

4.3 Fuel and Oxidizer Positive Controls

Various fuels and oxidizers, such as those listed in Table 1, can be used as positive controls. They will be prepared in a manner appropriate for the analytical technique being used.

4.4 Additional Positive Controls

Additional positive controls are prepared as necessary in order to identify components of mixed samples Redacted
They will be prepared in a manner appropriate for the analytical technique being used.

5 Sampling

Refer to the Sampling Procedures in the Explosives Quality Assurance Manual.

6 Procedure

Explosives chemistry personnel will:

Clean work surfaces thoroughly with an isopropyl alcohol solution or other appropriate solvent. Cover the clean work surface with a disposable material such as kraft paper. Refer to the Explosives Contamination Prevention Guidelines for additional details.

Use appropriate personal protective equipment (e.g., safety glasses, laboratory coat, and disposable gloves) when examining evidence. This is intended to protect the individual conducting the exam and to prevent contamination of evidence.

Review and understand all safety information contained in Section 11 prior to beginning the following procedures.

For each instrumental technique, refer to the Instrument Parameters and Reagent Preparation SOP for Performance Monitoring Protocol (PMP) information, instrument usage procedures, parameters, and reagent preparation information. Prior to evidence analysis, follow the PMP for the instrument to conduct a QA/QC check to verify the instrument's reliability and reproducibility from analysis to analysis.

6.1 Macroscopic/Microscopic Examination

Perform a macroscopic examination and note the homogeneity, color, and consistency of the unknown material.

When possible, separate the powder material if it contains grains of different sizes, colors, or shapes. It may be necessary to view particles under a microscope to aid in separation.

Examine the material under a microscope and note physical characteristics (e.g., homogeneity, color, grain size, grain shape, perforations, mixture, atypical material). Measure grain length, thickness, and diameter as necessary. Photographs of the material and relevant positive controls may be recorded.

- Commercial black powder is composed of black, irregularly-shaped grains, often with a glazed coating giving the surface a smooth appearance. The mixing of the potassium nitrate, charcoal, and sulfur is so complete that the individual components are not visible through a stereomicroscope. Improvised black powders may vary in appearance.

- Black powder substitutes vary in appearance based on manufacturing processes and formulation. For example, Pyrodex is a heterogeneous granular material composed of gray and white areas.

- Flash powder is generally gray or metallic in color and can vary from a visibly homogeneous mixture to a granular heterogeneous mixture. It is generally composed of clear to translucent crystals, which are the oxidizer(s), and silvery-metallic particles, which are the fuel(s).

- The pyrotechnic composition within flares generally has an off-white powdery appearance. The bulk of the flare consists of large and small translucent crystals, some being very pale yellow in color, interspersed with very small black or dark gray particles and sawdust. (Optional) After a hexane extraction, fibrous material visually consistent with wood may be seen under the microscope.

6.2 (Optional) Thermal Susceptibility Test

If sample size permits, place a small amount (~50 mg) of material on the tip of a spatula and heat with a lighter, torch, or match. Note the burn properties such as flame, smoke, and residue.

- Black powder and black powder substitutes will both burn rapidly with a flash and smoke and leave a residue.
- Flash powders will burn rapidly with a bright flash.
- A flare should produce a self-sustained reaction.
- Other pyrotechnics will burn with various effects including color, sound, heat, and smoke.

6.3 XRD Analysis

If sample size permits, grind a portion of the sample to a fine powder, as necessary, with a mortar and pestle and analyze by XRD.

- See Table 1 to determine example materials that may be identified by XRD.

Flares and pyrotechnics can contain oils and inorganic materials. A solvent (e.g., water, hexane) extraction may be necessary in order to define the inorganic phases properly via XRD. The material may be extracted with deionized water, the water evaporated from the extract, and the remaining solid residue analyzed by XRD.

6.4 SEM/EDS Analysis

If sample size permits, analyze a portion of the sample (bulk or ground) mounted onto an SEM sample holder to determine its elemental composition.

- See Table 1 to determine example elements that may be identified by SEM/EDS.

Solvent extractions may be necessary in order to identify the composition of individual components.

6.5 (Optional) FTIR Analysis

Analyze a portion of the sample (bulk or ground) on the FTIR spectrometer with an ATR or microscope attachment.

- See Table 1 to determine example materials that may be identified by FTIR spectroscopy.

Dried residues from water or methanol extracts of suspected black powder or black powder substitutes may be analyzed to determine the presence of Redacted

6.6 (Optional) Solids Probe MS/MS Analysis

For samples of suspected Pyrodex, Triple Seven, or some other black powder substitutes, analysis by solids probe MS/MS will determine the presence of benzoate and dicyanodiamide, which will differentiate these compounds from black powder.

Grind or crush a portion of the sample to a fine powder and extract it in approximately 300 µL of methanol for about an hour in a test tube. Retain a quantity of the methanol as a blank/negative control. Extract a positive control concurrently with the sample. Fill respective probe cups with the unknown methanol extract, the positive control extract, and the methanol blank and allow all the methanol extracts to evaporate. An oven may be used to speed the evaporation process.

Analyze the extracts by solids probe MS/MS (Electron Impact Ionization).

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6.7 (Optional) IC Analysis

Extract a portion of sample in up to 50 mL of deionized water. Retain an equal portion of water as a negative control. Where possible, plastic containers should be used during these procedures to avoid the leaching of ions from glassware. Flush a 0.2 µm filter mounted on a plastic syringe with deionized water. Flush portions of the negative control and the sample extracts through the prepared syringe filters into autosampler vials. An autosampler vial of unfiltered deionized water will be used as a blank.

Analyze the extracts by ion chromatography.

- See Table 1 to determine example cations and anions that may be identified by IC.

6.8 (Optional) Raman Spectroscopy Analysis

Analyze a portion of the sample (bulk or ground) on the Raman spectrometer in the macro compartment or using the microscope attachment.

- See Table 1 to determine example materials that may be identified by Raman spectroscopy.

Dried residues from water or methanol extracts of suspected black powder or black powder substitutes may be analyzed to determine the presence of Redacted

6.9 (Optional) GC/MS Analysis in Electron Ionization (EI) Mode

For samples of suspected flare material, a hexane extract may be used to determine the presence Redacted

Prepare a hexane extract of the suspected flare material, a hexane blank, and appropriate positive controls Redacted

Analyze the extracts by GC/MS (EI).

6.10 (Optional) GC/FID Analysis

For samples suspected of containing waxes and oils, a hexane extract may be used to determine their composition.

Prepare a hexane extract of the material, a hexane blank, and appropriate positive controls.

Analyze the extracts by GC/FID.

7 Decision Criteria

7.1 Instrumental Results

The following criteria will be met in order for a qualitative identification to be made. The identity of a material will be confirmed by comparison to a reference or known material, if available. Reference or known materials may be run concurrently with an unknown sample or may be previously analyzed on the instrument under the same parameters. A reference or known material will be analyzed by at least one spectroscopic technique used for comparison to an unknown material. All results should be verified using orthogonal techniques or alternate methods.

When a reference or known material is not available or when only reference data (e.g., from scientific literature, publications, or an instrument library) is used, a material may be reported as "consistent with" a substance.

7.1.1 Chromatography

Peaks should show good chromatographic characteristics, with reasonable peak shape, width, and resolution.

The retention time of the peak of interest should be within ±2% of that for a contemporaneously analyzed reference or known material for gas chromatography and ±5% for liquid chromatography.

The baseline signal-to-noise ratio (SNR) for an analyte should be greater than three to be considered a peak. The signal intensity for an analyte peak should be at least ten times greater than the intensity of any carryover or system peaks which may have been present in analyses just prior to the sample (e.g., blanks or negative controls).

7.1.2 Mass Spectrometry

The mass spectrum of the analyte of interest should compare favorably with that of a contemporaneously analyzed reference or known material.

Characteristic ion plots are reviewed to determine the potential presence of a target analyte. The absence of a primary ion indicates a non-detect.

7.1.3 XRD

The diffraction patterns from the questioned compound should compare favorably to the corresponding reference or known material.

If the unknown material is matched through a library search, a reference or known material may be analyzed for comparison, if available. Tentative identifications may also be confirmed through orthogonal techniques such as FTIR, Raman, SEM/EDS, or GC/MS.

7.1.4 SEM/EDS

Peaks in the EDS spectrum should exhibit a Gaussian peak shape and a minimum SNR of 3:1. The elemental composition of the questioned compound should compare favorably to the corresponding elemental composition of the reference or known material. Elemental assignments made by the software should be verified by the individual conducting the exam.

7.1.5 Other Tests

The results of all tests (e.g., visual inspections, FTIR, Raman, pH) should compare favorably to the corresponding reference or known material.

7.2 Material Identification

Samples less than several milligrams and grains lacking the physical characteristics of commercial black powder or black powder substitutes can be considered consistent with commercial or improvised (homemade) black powder, black powder substitutes, or pyrotechnics unless otherwise noted below.

7.2.1 Black Powder

A material can be identified as black powder if Redacted be confirmed, and if the material is not adulterated with other chemicals. Physical characteristics of black powder (e.g., glazed coating, uniform size, homogeneity), the source of the material (e.g., fuse, firework), and positive burn characteristics will aid in this determination.

7.2.2 Black Powder Substitutes

A material can be identified as a black powder substitute based on the visual characteristics, chemical composition, and positive burn characteristics in comparison to other known black powder substitutes used as reference or known materials. This identification may be limited in scope to where a specific black powder substitute product cannot be named, but the material is identified as a general low explosive black powder substitute.

A material lacking physical characteristics associated with black powder substitutes can still be identified by the presence of specific target compounds Redacted which are indicative of specific black powder substitutes.

7.2.3 Flash Powder

A material can be identified as a flash powder based on the visual characteristics, chemical composition, and positive burn characteristics producing a bright flash of light. The oxidizers and fuels that compose a flash powder should be compared to reference or known materials.

When a material has the visual characteristics and chemical composition of a flash powder but does not produce positive burn characteristics, it should be identified as a fuel/oxidizer mixture. These fuels and oxidizers should be compared to reference or known materials.

7.2.4 Flare

Flares have three distinct sections: the match head, the scratcher, and the main pyrotechnic material.

The match head of a flare can be identified based on the visual characteristics (typically a solid plug of material) and chemical composition. If enough material is present to break off a small

piece of the match head, then positive burn characteristics will aid in the identification. The oxidizers and fuels composing the match head should be compared to reference or known materials when available.

The scratcher of a flare can be identified based on the visual characteristics and chemical composition. The main chemical component in the scratcher is Redacted and should be compared to a reference or known material.

The main pyrotechnic material of a flare can be identified based on the visual characteristics Redacted chemical composition, and positive burn characteristics. Oxidizers and fuels present within the main pyrotechnic material should be compared to reference or known materials when available.

7.2.5 Pyrotechnics

A material can be identified as a pyrotechnic composition based on the visual characteristics, chemical composition, and positive burn characteristics producing pyrotechnic effects such as color, sound, heat, and/or smoke. The oxidizers and fuels that compose a pyrotechnic composition should be compared to reference or known materials.

When a material has the visual characteristics and chemical composition of a pyrotechnic composition but does not produce positive burn characteristics, it should be identified as a fuel/oxidizer mixture. These fuels and oxidizers should be compared to reference or known materials.

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

The identification of uninitiated black powder, black powder substitutes, or pyrotechnics may be limited by sample size. Several milligrams of uninitiated material are essential to microscopically observe the manufacturing characteristics.

11 Safety

Safety protocols, contained within the FBI Laboratory Safety Manual, will be observed at all times.

Take standard precautions for the handling of all chemicals, reagents, and standards. Take standard universal precautions for the handling of biological and potentially hazardous materials. Refer to the FBI Laboratory Safety Manual for proper handling and disposal of all chemicals. Personal protective equipment will be used when handling any chemical and when performing any type of analysis.

The handling of some explosive materials is hazardous due to potential ignition by heat, shock, friction, impact, or electrostatic discharge. Personnel should work with small quantities of material (such as a few grams) and properly store larger quantities in approved containers.

As a safety precaution, it should be noted that dark materials pose a hazard when being analyzed by Raman spectroscopy as they may be initiated by the laser. If this technique will be utilized, then the smallest possible sample amount and reduced laser intensities should be used to minimize the risk and avoid initiation.

12 References

FBI Laboratory Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

FBI Laboratory Operations Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

FBI Laboratory Safety Manual, Federal Bureau of Investigation, Laboratory Division, latest revision.

Explosives Quality Assurance Manual, Federal Bureau of Investigation, Laboratory Division, Explosives, latest revision.

Explosives Standard Operating Procedures: Chemistry, Federal Bureau of Investigation, Laboratory Division, latest revision.

Instrument Operations Manuals for the specific models and accessories used.

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Rev. #	Issue Date	History
2	10/04/2018	Administrative changes for grammar and clarity. Added Triple Seven components to section 2 and Table 1. Removed testmix components in section 4. Added location-specific PMP references to section 6. Added SAU IOG reference and modified IOSS reference.
3	12/16/2019	Changed line spacing after section 6.7. Removed sampling plan from section 5. Removed SAU Chief and QA from approval lines. Removed unit references to PMPs.

Approval

Redacted - Signatures on File

Explosives Unit Chief Date: 12/13/2019

TL Approval

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