Fuel and Oxidizer Mixture Analysis

Table of Contents

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1 Introduction

Fuel and oxidizer (FOX) mixtures are commonly encountered in the analysis of explosives. These types of mixtures can be commercially purchased or improvised. Commerical products include black powder, black powder substitutes, pyrotechnic mixtures, flares (fusees), exploding targets, and some blasting explosives. Compositions of improvised mixtures can be nearly limitless with some mixtures containing only a single fuel and a single oxidizer, while others can be complex with multiple fuels and/or oxidizers. Other non-energetic additives may be present in some FOX mixtures (e.g., quartz, clay bentonite, calcium carbonate). Common compositions of fuel and oxidizer mixtures are listed in Table 1.

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

Commercial black powder is composed of potassium nitrate, charcoal, and sulfur in a ratio of approximately 75:15:10 and may be found in several Fg grades. F denotes “fine” and g denotes “glazed.” Fg powders are larger in grain size than FFFFg powders, which are comprised of extremely fine grains. Improvised or homemade black powders contain similar ingredients; however, they may be composed of different ratios and granular morphologies.

Pyrodex and Triple Seven are commercial black powder substitutes manufactured by Hodgdon Powder Company. Pyrodex is composed of potassium nitrate, potassium perchlorate, sodium benzoate, dicyanodiamide, sulfur, and charcoal and is available in various grain sizes and pellet forms. Triple Seven is composed of potassium nitrate, potassium perchlorate, sodium benzoate, dicyanodiamide, charcoal, and 3-nitrobenzoic acid.

Other black powder substitutes include, but are not limited to, Golden Powder, Black Mag, Black Canyon, Clean Shot, Clear Shot, and American Pioneer. Their chemical components may include, but are not limited to, ascorbic acid, charcoal, dicyanodiamide, fructose/sugar, 3-nitrobenzoic acid, potassium nitrate, potassium perchlorate, sodium benzoate, and sulfur.

A pyrotechnic is a mixture of chemicals 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. Oxidizers include, but are not limited to, barium nitrate, iron oxide, potassium chlorate, potassium nitrate, potassium perchlorate, or strontium nitrate. Fuels include, but are not limited to, aluminum, magnesium, magnalium (aluminum/magnesium alloy), sulfur, antimony trisulfide, sugar, or carbon.

Flash powder is generally gray or metallic in color varying from a visibly homogeneous mixture to a granular heterogeneous mixture. Flash powder is typically composed of a strong oxidizer such as potassium chlorate or potassium perchlorate and a metallic fuel such as aluminum. 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 or heat 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.

Ammonium nitrate (AN) is a commonly encountered oxidizer in commercial exploding targets (regularly paired with a metal fuel), commercial blasting explosives (paired with nitromethane or fuel oil), and in improvised mixtures. AN is generally produced in a prilled form for commercial applications. When fertilizer grade AN is mixed with calcium carbonate or dolomite (calcium magnesium carbonate) it can be referred to as calcium ammonium nitrate (CAN) fertilizer.

Table 1: Example compositions of FOX mixtures and products

Type	Example Composition
Black Powder	KNO_3, S, charcoal
Pyrodex	KNO_3, S, charcoal, $KClO_4$, sodium benzoate, dicyanodiamide
Triple Seven	KNO_3, charcoal, $KClO_4$, sodium benzoate, dicyanodiamide, 3-nitrobenzoic acid
Black Powder Substitutes (multiple formulations)	KNO_3, S, ascorbic acid KNO_3, $KClO_4$, ascorbic acid KNO_3, charcoal KNO_3, ascorbic acid
Flash powder	$KClO_3$, $KClO_4$, Al, Mg
Flare or fusee	Match head: Liquid shellac, $Sr(NO_3)_2$, SiO_2, charcoal, $KClO_4$, $KClO_3$, wood flour, marble dust Scratcher: Lacquer, pumice, red phosphorus Main pyrotechnic: $Sr(NO_3)_2$, S, $KClO_4$, sawdust, paraffin oil, fuel oil, corn starch, stearic acid
Pyrotechnics	Oxidizers: $Ba(NO_3)_2$, Fe_2O_3, $KClO_3$, $KClO_4$, KNO_3, $Sr(NO_3)_2$ Fuels: Al, Mg, magnalium, S, Sb_2S_3, C, sugar
ANFO	NH_4NO_3, fuel oil
Exploding targets	Oxidizers: NH_4NO_3, $KClO_3$, $KClO_4$ Fuels: Al, Mg, magnalium, S

2 SCOPE

This procedure describes the general process for the analysis of uninitiated FOX mixtures and the identification of their components. This procedure is suitable for bulk samples which are suspected of being a FOX mixture containing solid oxidizers and applies to caseworking personnel conducting work in explosives chemistry analysis. Mixtures containing a liquid oxidizer (e.g., hydrogen peroxide) are outside the scope of this procedure. In addition, FOX components may be present within a more complex improvised mixture containing organic explosives. Analyze these mixtures with the Identification of General Unknowns technical procedure.

3 EQUIPMENT

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

3.1 Equipment

- SEM stubs or carbon planchets with liquid adhesive (e.g., Duro-tak), carbon adhesive tabs, or aluminum or copper tape
- XRD sample holders (zero background holder with or without depression)
- General laboratory supplies

3.2 Instruments

- 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)
- Headspace gas chromatograph with mass spectrometer (HS-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)
- X-ray diffractometer (XRD)

3.3 Chemicals/Reagents

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

4 STANDARDS AND CONTROLS

Refer to the Explosives Quality Assurance and Operations Manual for details regarding verification of reference materials. Testmix components and preparation instructions are recorded in the applicable instrument performance documents. Refer to the Instrument Parameters and Reagent Preparation procedure for information regarding other positive controls relevant to this procedure. Refer to the Fire Debris and Ignitable Liquid Analysis procedure for ignitable liquid reference material information (e.g., fuel oil positive control).

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 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.

4.3 Additional Positive Controls

Additional positive controls are prepared as necessary in order to identify components of mixed samples (e.g., silicon dioxide, calcium silicate, collagen, dye, wax as present in a match head). 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 and Operations Manual.

6 PROCEDURE

Explosives chemistry personnel will:

Consult the Examination Plan to determine if exams by other disciplines/subdisciplines will be performed on the items to be tested (e.g., fuses). If certain aspects of the explosives chemistry testing may affect subsequent exams, then the steps performed may need to be modified and/or consultation may be necessary with other discipline/subdiscipline personnel.

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 Quality Assurance and Operations Manual for additional details regarding explosives contamination prevention.

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.

For each instrumental technique, refer to the Instrument Parameters and Reagent Preparation procedure for instrument usage procedures, parameters, and reagent preparation information. Prior to evidence analysis, follow the applicable instrument performance document to conduct a performance check.

6.1 Macroscopic/Microscopic Examination

Perform a macroscopic examination and note the physical characteristics (e.g., homogeneity, color, consistency) of the unknown material.

When possible, separate the material if it contains grains of different sizes, colors, or shapes or appears to have a liquid phase. 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). 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 thorough 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.

- AN mixtures may contain round spheres or prills. AN may also be present in powder form.

- If present, describe the liquid phase and analyze separately, if possible. Some liquid fuels may have a strong hydrocarbon-like odor. This should be noted if readily apparent, but do not intentionally smell any sample submitted for analysis.

    - IMPORTANT - If liquid fuels are suspected based on visual examination and/or olfactory observations, FTIR analysis is required of the bulk material (or separated liquid). In addition, either GC/FID or HS-GC/MS is required. Refer to applicable sections 6.5, 6.7, 6.8, and 6.9 below.

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. Some mixtures may require prolonged heating (e.g., thermites) to result in a positive test result.

- Black powder and black powder substitutes will both burn rapidly with a flash and smoke and leave residue.

- Flash powders will burn rapidly with a bright flash.

- A flare mixture should produce a slower self-sustained reaction than other pyrotechnic mixtures.

- Other pyrotechnics will burn with various effects including color, sound, heat, and smoke.

- General low explosive mixtures should burn rapidly with a self-sustaining reaction (with or without smoke and/or residue).

- Some mixtures may not produce an energetic reaction but could physically change (such as melting and/or bubbling).

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. CAUTION – some FOX mixtures are friction sensitive. Only use the amount needed for analysis with minimal pressure.

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. However, ionic rearrangement should be considered prior to conducting water extracts of mixtures with multiple oxidizers (e.g., potassium perchlorate and barium nitrate).

Some mixtures may contain hydrocarbon components (e.g., oils, petroleum jellies, waxes) that can be extracted with hexane. Analyze these extracts via GC/FID as described in section 6.7.

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.

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

The production coatings and fillers of AN prills can be used to compare different samples/sources of AN for likeness.

6.5 (Optional) FTIR Analysis

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

Dried residues from water or methanol extracts of suspected black powder or black powder substitutes may be analyzed to determine the presence of sodium benzoate, dicyanodiamide, potassium perchlorate, and potassium nitrate.

FTIR analysis of bulk mixtures will aid in determining the presence of liquid fuels.

6.6 (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.

Dried residues from water or methanol extracts of suspected black powder or black powder substitutes may be analyzed to determine the presence of sodium benzoate, dicyanodiamide, potassium perchlorate, and potassium nitrate.

6.7 (Optional) GC/FID Analysis

For samples suspected of containing hydrocarbon fuels, prepare a hexane extract of the material, a hexane blank, and appropriate controls. Analyze the extracts by GC/FID.

If the results of the FID analysis reveal that the carbon-range distribution falls below ~C25, the extracts may be analyzed via GC/MS as described in step 6.8.

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

For samples containing a hydrocarbon profile distribution under ~C25, these extracts can be further analyzed by GC/MS in EI mode (FIRE method) for classification of the hydrocarbon present. Refer to the Fire Debris and Ignitable Liquid Analysis procedure for the FIRE method parameters.

6.9 (Optional) HS-GC/MS Analysis in EI Mode

If a light or volatile liquid fuel is suspected upon visual examination, olfactory, or FTIR analysis, place a small amount of material (either separated liquid or original sample) into a 20 mL headspace vial for analysis on HS-GC/MS. Some volatile liquids of interest (e.g., nitromethane) are miscible in water. A dilution using deionized water may be needed for proper instrument response. If diluting, make an approximately 200 ppm solution using the original sample or a 0.02% (v/v) solution if using a separated liquid. A sealed empty headspace vial or a headspace vial containing deionized water (whichever is applicable) serves as a negative control.

6.10 (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.

7 Decision Criteria

Refer to the Explosives Chemistry Report Writing Guidelines and the Report Wording Examples for Explosives Chemistry Analysis document (level 4) for additional details regarding reporting of FOX mixtures.

7.1 Instrumental Results

Refer to the Instrument Decision Criteria for Explosives Chemistry Analysis procedure for details regarding the acceptance of data generated using the instruments and methods described above.

7.2 Material Identification

In general, positive burn characteristics must be observed to identify a low explosive mixture or product as long as enough material is present to conduct the thermal susceptibility test. Refer to section 6.2 for expected burn properties based on the specific material. When a material has the chemical composition of a low explosive mixture or product but does not produce positive burn characteristics, it should be identified as a fuel/oxidizer mixture. A caveat can be included stating that if the mixture is combined appropriately, a low explosive (or incendiary) mixture could be formed.

7.2.1 Black Powder

The minimum identification requirements for black powder are:

- Visual characteristics of the grain(s)
- Confirmation of components listed in Table 1, except charcoal.

If physical grain morphologies are not present, the source of the material (e.g., fuse, firework) will be considered prior to identification. If it is a commercial source (e.g., fuse, firework) and the other criteria are met, the material can be identified as black powder without grain morphology. If the source is unknown/non-commercial, the material can be identified as a low explosive mixture.

If not enough material is present to conduct a thermal susceptibility test and grain morphology is not present or the source of the material is unknown/non-commercial, then the material may be reported as consistent with a low explosive mixture.

7.2.2 Black Powder Substitutes

The minimum identification requirements for Pyrodex and Triple 7 are:

- Confirmation of the components listed in Table 1, except charcoal. The presence of sodium benzoate, dicyanodiamide, and 3-nitrobenzoic acid do not need to be confirmed with an orthogonal technique in order to identify the product.

The identification of other substitutes 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. This is due to other substitutes having compositions that cannot be differentiated by this procedure.

7.2.3 Low Explosive Mixtures

The minimum identification requirements for a low explosive mixture are:

- Confirmation of at least one oxidizer, except ammonium nitrate, and a solid fuel. Examples are provided in Table 1.
- A positive thermal susceptibility test.

7.2.4 Pyrotechnic Mixtures

The minimum identification requirements for a pyrotechnic mixture are:

- Confirmation of at least one oxidizer, except ammonium nitrate, and a solid fuel. Examples are provided in Table 1.
- A positive thermal susceptibility test.

Pyrotechnic mixtures are low explosive mixtures that produce pyrotechnic effects such as color, sound, heat, and/or smoke. These mixtures can be identified as pyrotechnic mixtures or low explosive mixtures (examiner discretion).

Flash powder is a common name for a type of low explosive mixture that produces a bright flash of light. These mixtures can be identified as flash powders or low explosive mixtures (examiner discretion).

7.2.5 Incendiary Mixtures

Incendiary mixtures are low explosive pyrotechnic mixtures that produce very high heat but little to no gas. Thermite is a common name for these mixtures.

The minimum identification requirements for incendiary mixtures are:

- Confirmation of a metal oxide (e.g., iron oxide, copper oxide) and a metal or elemental fuel (e.g, aluminum powder, sulfur)
- A positive thermal susceptibility test with little to no gas production.

7.2.6 Flares (Fusees)

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

The match head of a flare is a low explosive pyrotechnic mixture that is typically a plug of material. This part of the flare will follow the identification requirements for low explosive pyrotechnic mixtures.

The scratcher of a flare can be identified based on the visual characteristics and chemical composition. The main chemical component in the scratcher is red phosphorus.

The minimum identification requirements for the main pyrotechnic material (body) of a flare are:

- Confirmation of at least one oxidizer and fuel listed in Table 1 in addition to material visually consistent with wood meal or saw dust.
- A positive thermal susceptibility test.

Oxidizers and fuels present within the main pyrotechnic material should be compared to reference or known materials when available.

7.2.7 High Explosive Mixtures

Some FOX mixtures can create high explosives. These mixtures generally contain ammonium nitrate or potassium chlorate as an oxidizer. In addition, these mixtures usually do not produce positive thermal susceptibility results (except for a physical change in the material).

The minimum identification requirements for a high explosive FOX mixture are:

- Confirmation of ammonium nitrate or a chlorate-based oxidizer (e.g., potassium chlorate, ammonium chlorate) and at least one fuel.
- Burn characteristics that do not support identification as a low explosive material.

- Range testing, confirming the reactivity of the mixture.

Often range testing is not available or applicable due to submitted amounts. In these circumstances, the material may be reported as consistent with a high explosive mixture.

8 Measurement Uncertainty

Although infrequent, the mass of a crude material may be requested by the contributor. When requested, refer to the Explosives Quality Assurance and Operations Manual for information regarding measurement uncertainty of these results.

9 Limitations

This procedure does not address the analysis and limitations of explosive residue examinations.

When an item is tested, a representative sample is tested (if not the whole item). However, the results of the analysis only pertain to the portion of the item tested.

The identification of FOX mixtures may be limited by sample size. If specific identification requirements cannot be met, materials may be reported as "consistent with" a particular explosive type if analytical results are supportive.

Only examiners qualified and authorized in fire debris and ignitable liquid analysis may identify a class of ignitable liquid (e.g., heavy petroleum distillate, gasoline). Examiners not qualified and authorized for this analysis may only report general profile characteristics (e.g., oil, wax, petroleum jelly).

10 Safety

The handling of 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.

11 References

ASTM E3196-21, Standard Terminology Relating to the Examination of Explosives, ASTM International, West Conshohocken, PA, 2021 (or latest version).

ASTM E3253-21, Standard Practice for Establishing an Examination Scheme for Intact Explosives, ASTM International, West Conshohocken, PA, 2021 (or latest version).

12 Revision History

Revision	Issued	Changes
00	09/30/2022	Original document issued that combines Ammonium Nitrate-Based Binaries Analysis (rev. 4) and Black Powder, Black Powder Substitutes, and Pyrotechnics Analysis (rev. 3) procedures.