Ammonium Nitrate-Based Binaries Analysis

1 Scope

These procedures describe the general process for the analysis of bulk ammonium nitrate-based binaries and the identification of their components. These procedures are suitable for bulk samples which are suspected of being a binary explosive mixture containing ammonium nitrate as the oxidizer and a fuel such as Redacted These procedures apply to caseworking personnel conducting work in explosives chemistry analysis.

2 Introduction

A common class of materials which include binary explosives and simple oxidizer/fuel mixtures based on ammonium nitrate (AN) as the oxidizer are frequently encountered in the FBI Laboratory. Redacted

3 Equipment/Materials/Reagents

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

3.1 Equipment

- 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) with optional digital camera
- Raman spectrometer with macro compartment or microscope attachment

- Scanning electron microscope with energy dispersive X-ray spectrometer (SEM/EDS)
- X-ray diffractometer (XRD)

3.2 Materials

- Autosampler vials and caps
- Disposable plastic syringes
- Kraft paper
- Mortar and pestle
- Spatula
- Syringe filters (0.2 µm nylon)
- Various disposable glassware and plasticware
- XRD sample holders (zero background holder with or without depression)

3.3 Reagents/Solvents/Reference Materials

- Carbon disulfide (reagent grade)
- Deionized water (18.2 MΩ)
- Hexane (reagent grade)
- Isopropyl alcohol (70% commercial product)
- Nitrogen (high purity)

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.

- Redacted

4.1 Additional Positive Controls

Additional positive controls may be prepared as necessary in order to identify components of mixed samples (e.g., AN, icing sugar, aluminum). They may be prepared in a manner appropriate for the analytical technique being used.

5 Sampling

Refer to the Sampling Procedures SOP 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, disposable gloves) when examining evidence. This is intended to protect personnel conducting the examination 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's reliability and reproducibility from analysis to analysis.

6.1 Microscopically observe the material noting any round spheres or prills of AN. AN may also be present in powder form Redacted
Describe the liquid phase and analyze separately, if present.

6.2 (Optional) Analyze a portion of the sample on the FTIR spectrometer to assist in identifying AN and any additional sources of fuel or other materials.

6.3 (Optional) Analyze a portion of the sample on the Raman spectrometer to assist in identifying AN and any additional sources of fuel or other materials.

6.4 (Optional) SEM/EDS can be used to analyze any fillers or inorganic coatings associated with the production of AN. Redacted
The SEM/EDS results for AN should detect nitrogen and oxygen. Magnesium, calcium, aluminum, silicon, or sulfur may be detected as a result of the manufacturing process of prilled AN.

6.5 (Optional) A small amount of sample can be screened on the Headspace GC/MS for volatile compounds. Small items of evidence may also be screened if the item can fit within a 10

or 20 mL vial. A 0.5 mL sample of the headspace GC/MS volatiles testmix in an autosampler vial serves as a positive control. A sealed blank autosampler vial serves as a negative control. The evidence may be heated up to 90°C, prior to headspace sampling, based on the individual's judgment on how much heating is necessary and for how long. The situation may be that ambient temperature is sufficient, or only gentle heating.

6.6 If indicated by visual appearance, FTIR or Raman analysis, or other preliminary data, the sample can be washed with Redacted

Extract with just enough solvent to allow swirling or agitation over the material. The extract may be filtered and/or concentrated using heat and/or nitrogen/filtered air as appropriate. The final volume of the extract will depend on the amount of co-extracted material from the sample as well as the amount of extracted product present. If filtering and/or extract concentration is required, a negative control will also be prepared in the same manner. Transfer the solvent to an autosampler vial for analysis by GC/FID and/or GC/MS in electron ionization (EI) mode.

6.7 A portion of the prills and/or powder will be examined by XRD (before or after the hexane rinse). For XRD, a spatula quantity of prill or powder material is ground to a fine powder then spread onto an XRD sample holder (zero background with or without depression) for analysis. The results are compared to a sample of known AN.

6.8 (Optional) Dilute a spatula tip quantity of the specimen in up to 50 mL of deionized water. Retain an equal portion of the water as a negative control. Plasticware containers should be used throughout these procedures to avoid leaching of ions from glassware. Prepare a plastic syringe and 0.2 µm nylon filter (mounted on a plastic syringe) by flushing with deionized water. Flush portions of the negative control and then the sample through the filter and into their respective autosampler vial for IC analysis to determine the presence of any anions or cations. The cations and anions testmixes serve as the positive controls.

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. 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

An AN binary can be identified based on the visual characteristics and chemical composition (AN in addition to a fuel component). This combination is required to indicate a combination of materials which may be capable of causing an explosion.

The AN and fuel components can be identified when the analytical results from two orthogonal techniques corroborate each other. The AN and fuel components should be compared to reference or known materials.

Redacted

8 Calculations

Not applicable.

9 Measurement Uncertainty

Not applicable.

10 Limitations

10.1 The presence of the ammonium ion or AN does not constitute confirmation of ANFO or other ammonium-based binaries as there are many explosive and fertilizer products that contain AN as an ingredient.

10.2 The identification of uninitiated material may be limited by sample size. Identification of residues from initiated material is possible at detection levels of several micrograms; however, a specific combination of compounds is mandatory to establish residues as consistent with an explosive mixture. Refer to the Explosive Residue Analysis SOP.

11 Safety

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

Standard precautions will be taken for the handling of all chemicals, reagents, and standards including 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 (such as a few grams) and properly store larger quantities in approved containers.

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, latest revision.

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

Instrument Operations Manuals for the specific models and accessories used.

Cooper, P. and Kurowski, S. *Introduction to the Technology of Explosives*, VCH, New York, 1996.

Rev. #	Issue Date	History
3	10/04/2018	Administrative changes for grammar and clarity. Removed testmix components in section 4. Added location-specific PMP references to section 6. Removed PLM microscopy from section 6.2. Reworded section 6.6 examples. Redacted Added section 7 Decision Criteria. Added SAU IOG reference and modified IOSS reference.
4	12/16/2019	Changed title to Ammonium Nitrate-Based Binaries Analysis. Clarified that heat and/or nitrogen/filtered air can be used as appropriate. Removed sample selection from section 5. Removed SAU Chief and QA from approval lines. Removed unit references to PMPs.

Redacted - Signatures on File

Approval

Explosives Unit Chief Date: 12/13/2019

TL Approval

Explosives Chemistry
Technical Leader Date: 12/13/2019